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# POLLUTION PROBLEMS AND SOLUTIONS IN THE NON-FERROUS METALS INDUSTRY *

Prepared by

the UNIDO Secretariat

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Glossary of terms

ACGIH American Conference of Governmental Industrial Hygenists. An organization including professional personnel in governmental agencies and educational institutes whose aim is the development of administrative and technical aspects of workers' health protection and the promotion of standards and techniques in industrial hygiene. Its Committee on Threshold Limit Values keeps under constant revision the permissible concentration of a list of 400-500 substances.

CWPB Central-worked pre-bake. It refers to electrolytic cells for aluminium production in which the graphite anodes are manufactured (baked) in a separate part of the plant. In addition, alumina feeding to the cell takes place by breaking the cryolite solid crust in a "central" space placed between two lines of anodes.

KWhr DC 1 Kilowatt x 1 hour of direct current.

$Nm^3$ Normal cubic meter. The gas content of one cubic meter space measured at standard temperature and pressure, i.e. 0°C and 1 atmosphere.

SWPB Side-worked pre-bake. It refers to electrolytic cells for aluminium production. Similar, in principle, to the CWPB (see above), the SWPB cells have an alumina feeding system which consists of breaking the cryolite solid crust around the whole circumference of the anode complex.

TSS Total suspended solids.

TWA Time-weighed average. It refers to the concentration of pollutants in the air averaged over a period of time.

## 1. INTRODUCTION

The non-ferrous metal industries considered in this study: aluminium, nickel, copper, lead, zinc and tin, play a major role in the economy of several industrialized and developing countries. Unfortunately, they are also among those industrial sectors which entail emission or release of enormous amounts of pollutants into the environment. Each one of the steps required for the production of a metal can be associated, to a certain extent, with a detrimental impact on the environment. This impact is made even more significant by the sheer size of the industry and by the type of pollutants generated. To take a specific case as an example, one single nickel/copper production facility releases through its stacks some 2,500 tons of sulphur dioxide into the atmosphere every day.

Smelting of sulphide ores as in the case of nickel, copper, lead and zinc is typically associated with two potential environmental problems, namely dust and fume emissions, and sulphur dioxide emissions. The former problem may become even more significant if the dust contains appreciable amounts of harmful heavy metals such as lead, cadmium, and mercury or elements such as arsenic, antimony and bismuth. The latter hazard, $SO_2$, has been found to be directly responsible for the acid rain problem which has already caused significant environmental damage. Modern smelters can be equipped with devices which collect dust and fumes and convert sulphur dioxide to usable chemicals, thus greatly reducing their negative environmental impact. In addition, new smelting technologies already exist or are undergoing trial tests, which reduce the amounts of pollutants produced or produce pollutants which are amenable to removal or conversion to harmless chemicals. Yet older smelters remain a potentially large source of contamination especially since they can hardly be retrofitted to significantly reduce pollution.

Smelting of oxidized ores as in the case of aluminium, nickel, and tin is associated with dust emissions or different (such as fluoride emission) kinds of environmental problems.

Because of these aspects it is necessary that the non-ferrous metal industries keep increasing their control efforts to minimize the environmental impact caused by their activities. Already in the past decades new technological innovations coupled with some major changes in the market structure of the business and new more stringent environmental regulations have produced significant shifts in strategies adopted by the industry with positive environmental implications. Hopefully this trend will continue in the future.

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# 2. ALUMINIUM

## 2.1 Pollution control technologies for aluminium production plants

### 2.1.1 Pollution control during alumina production

Since red mud (alkaline bauxite residue) is the largest quantity of effluent from an alumina plant the methods used for its disposal, impoundment, or storage are especially important.

The envisaged potential impacts caused by land disposal methods are:[1/]

(1) Seepage of alkaline liquor into the ground. Possible contamination of ground water may result.

(2) Spills due to cracked pipelines or containment dam failure.

(3) Dust pollution in arid regions.

(4) Reduction of availability of usable land.

(5) Aesthetic impact.

As a result, the most effective pollution control (or containment) methods consist of the proper siting of the plant and disposal area, careful construction and monitoring of the impoundment area, and minimization of seepage through use of sealant for lining of the impoundment area. At sea, the discharged liquid residue rapidly reacts with the magnesium contained in sea water. This chemical reaction produces a finely divided precipitate which may be harmful to marine life. Hence, this disposal method should be used only as a last resort. Disposal in shallow water should be avoided altogether. Should disposal at sea be dictated by a dramatic shortage of land, a careful environmental impact study should be carried out, followed by intensive monitoring. This disposal method will be more expensive than disposal on land.

### 2.1.2 Pollution control during aluminium production

In the Hall-Heroult process, gaseous waste streams are produced from pot rooms, pot lines, green anode and anode baking plants, and cast-house. Most plants effectively collect and remove the different pollutants. Therefore very little is released to the atmosphere. The different emission sources will now be examined.

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1/ "Guidelines for the Environmental Management of Alumina Production", UNEP, Industry and Environment Guidelines Series.

Pollution control of fumes produced in the electrolytic cells

The fumes produced in the cells must be first efficiently collected. In prebaked anode cells this is done through hoods made up of several shields. Each time an anode is replaced only two or three of these shields must be removed. As a result, collection efficiency does not drop significantly during this operation. It is estimated that only 20 per cent of the total fluoride generated in the cells is not collected by the hoods during the anode change.[2/] As for Söderberg pots, attempts (not completely effective) have been made to use panels above the skirt in order to collect the fumes which might escape.[3/] In all cases good fume collection is essential to protect the worker's health from exposure to toxic pollutants. After collection, the coarser particles in the fumes are removed through cyclones. Typical removal rates are shown in table 2.1.

Table 2.1. Dust removed by cyclones

| Location of plant | Dust collected kg dust/t Al | Pressure loss (mm water gauge) | Content of dust | |
|---|---|---|---|---|
| | | | $Al_2O_3$ (per cent) | F (per cent) |
| USA | 38.5 | 76 | 60 | 10 |
| Fed.Rep.Germany | 32.0 | 100 | 64-74 | 15-20 |
| New Zealand | 47.0 | 160 | 70 | 9.2 |
| France | 12.37 | 40 | 60-80 | 10-19 |

Source: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 51.

The fumes are then passed through wet or dry cleaning devices. Both have a high fluoride removal efficiency. Some wet scrubbers are less efficient for sub-micron particles removal. Wet systems consist of contacting devices where the fumes are scrubbed with caustic soda, lime or soft water. In the process, the fluorides are removed as cryolite or $CaF_2$. In addition, $SO_2$ may be also partially removed, thus limiting air pollution. On the other hand, the scrubbing solution requires some processing before being discharged into the environment. In the dry process the fume collected from prebake pots is

2/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

3/ Aluminum Péchiney, Ph. Le Cardinal, Hooding of Söderberg Pots in Saint-Jean-de-Maurienne Plant, AIMA, 1976.

contacted in a reactor at 100°C with the alumina which is going to be fed to the pots. The reactor is a fluidized bed or pipe where alumina is injected concurrently with the gas. Although contact time is only about one second, HF (in concentration of 100-200 mg F/$Nm^3$) is effectively removed (99 per cent efficiency). The alumina particles entrained by the cleaned gas are then removed by a fabric filter. All alumina is fed back to the pots.

Pollution control for green anode pots

All equipment (pitch melter, paste mixer, grinder, screener, anode forming machine) should be enclosed and the tar fume processed before being exhausted. Wet or dry methods can be used.

Pollution control for the anode bake oven

Pollutants generated are $SO_2$, nitrogen oxides (as combustion products), tar fumes, carbon dust, and fluorides (from anode butts). The solid particles can be collected by an electrostatic precipitator, wet scrubbing or dry alumina contacting. Nitrogen oxides and the remaining $SO_2$ usually escape to the atmosphere.

Pollution control for the cast house

Fluxing fumes containing fluorides and dust are usually produced in limited amounts. These fumes can be harmful to the workers and attention should be paid that their concentration in air is always low. If chlorine gas is used for degassing of the liquid metal the fume should be scrubbed with alkaline solutions.

Pollution control of liquid effluents

The water used in wet scrubbing is the most polluted. It contains fluorides, sulphates and, in the case of Söderberg pots, hydrocarbons. The water should be treated. Fluorides are usually recovered as cryolite.

Pollution control of solid wastes

Storage and disposal of anode butts and spent cell linings must be provided. During outdoor storage, some fluorides and cyanide may be leached out by runoff water, and cause soil contamination. Consequently, the spent material should be transformed into non-hazardous waste before final disposal.

## 2.2 Retrofitting of existing plants to reduce pollution

Because of the technological advances in aluminum production and environmental control, significant progress was made over the past 30 years in reducing the amount of fluorides produced by smelting plants. As an example, some 12-25 kg of total fluorides were emitted per ton of Al produced by a typical smelting plant in 1950. This figure was lowered to 0.5-1 kg in 1985. The first step in retrofitting should be to fit hoods to the existing pots for effective fume collection. Table 2.2 shows the results obtained by using different collection techniques.[4/]

Table 2.2. Different fume collection techniques

| Potline | Amperage KA | Collection technique | Evacuation flow rates $Nm^3/s/pot$ | Evacuation flow rates $Nm^3/t\ Al\ 10^5$ | Collection efficiency (per cent) |
|---|---|---|---|---|---|
| CWPB | 150 | Multiple shielded hood | 1.1 | 0.9 | 95-99 |
| CWPB | 180 | Multiple shielded hood | 2.0 | 1.3 | 97-99 |
| SWPB | 130-140 | Hood with one panel on each side | 0.9-1.2 | 0.8-1.0 | 80-90 |
| SWPB | 90 | Local hood | 0.1 | 0.13 | 65-75 |
| VSS | 100-120 | Skirt with one or two burners | 0.13 | 0.15 | 65-85 |

Source: "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 25.

A further step would be to use cyclones for coarse dust removal and recycle the dust back to the pots. An additional step would then be to install scrubbers after the cyclones. This would reduce the fluoride particle

4/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

content and HF by about 50 per cent (cyclone alone) and 95 per cent (cyclone plus scrubber) respectively. New, larger plants (200,000 tons Al/year) should be equipped with a dry process system and stack. Table 2.3 summarizes this information. It should be noted though that, in general, industry does not find it convenient to retrofit old smelters with adequate pollution control equipment. Consequently, some industries and governments have decided to launch a modernization and plant replacement program.[5/]

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5/ "The Aluminium Industry and the Environment", UNEP, Industry and Environment, July, August, September 1979, Vol. 2, No. 3.

Table 2.3 Pollution control technologies for aluminum production plants of different capacities (central worked prebake pots only; 97 per cent collection efficiency)

| Step No | Annual capacity | Evolution kg/t al | | | | | Cleaning technology | Emission kg/t al | | | | | Emission |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Total | Vent. air | Collected fume | | | | Total | Vent. air | Stack fume | | | |
| | | Ft | Ft | Fg | Fp | Ft | | Ft | Ft | Fg | Fp | Ft | Ft per year |
| 1 | 50,000 | 18 | 0.54 | 8.73 | 8.73 | 17.46 | Cyclone + stack | 14.51 | 0.54 | 8.73 | 5.24 | 13.97 | 725 |
| 2 | 50,000 | 18 | 0.54 | 8.73 | 8.73 | 17.46 | Cyclone + wet scrubber + stack | 3.60 | 0.54 | 0.44 | 2.62 | 3.06 | 180 |
| 3 | 200,000 | >20 | 0.6 | 10.67 | 8.73 | >19.4 | Dry process + stack | 0.95 | 0.6 | - | - | 0.35 | 190 |

Source: "Environmental Aspects of Aluminum Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 50.

## 2.3 Pollution control costs

According to reference 50 the cost of establishing an impoundment area (in Hungary) is about 0.3-0.4 $US/m$^3$ of storing capacity provided that the sludge of fly ash coming from the power plant is used for building the dikes. If earthen dikes are built the cost rises to 0.7-0.8 $US/m$^3$. Operating costs run between 0.1 and 0.15 $US/ton of alumina depending on the distance between the plant and the impoundment area.[6]

A report prepared by the International Primary aluminium Institute (IPAI)[7] and other studies show that pollution control costs for new plants are considerably lower than costs of retrofitting existing plants.

The data in table 2.4 provide separate operating and capital costs and recovery credits (where applicable) for different types of pollution control systems.[8] They were calculated on the basis of a plant with a production capacity of 50,000 ton/year of aluminium. To give some idea of retrofitting costs, the addition of a secondary wet scrubber to an existing plant would cost at least double if a primary scrubber had been installed first. The average capital investment for fluorine control is an additional seven per cent of the initial production plant capital cost (on the basis of a cost of $US 2,000 per ton of installed production capacity). The additional operating costs would range between 0.8 and 6.6 per cent.

Another survey was conducted by OECD in 1977 and covered aluminium production plants in the USA, Canada, Japan and Norway.[9] The report concluded that capital construction cost for new plants was $US 2,300 while operating costs varied between $US 780 and $US 1,040 per ton of Al. Based on these figures the report concluded that the maximum additional cost of pollution control was 6.3 per cent of total production costs while the corresponding operating costs were in the range of 2.2-7.2 per cent of the initial capital investment. For existing potrooms the report estimated the additional cost for pollution control to be $US 17.5 per ton of installed Al capacity. The corresponding operating costs were estimated to be $US 22.4 per ton of Al with a considerable standard deviation of $US 18.7.

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6/ Anon, "Information on the Environmental Aspects of Alumina Production in Hungary", Document ALU 80/495C, Budapest, 1980.

7/ International Primary aluminium Institute Report.

8/ Atkins, M.H. and J.F. Lowe. The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979, p. 36.

9/ "Pollution Control Costs in the Primary Aluminium Industry", O.E.C.D., Paris, 1977, p. 36.

Pollution removal efficiencies obtained by Rush, Russel and Ireson [10] using comparatively new methods, such as the injected alumina dry method, produce very good removal efficiencies at a relatively low cost. Other systems of pollution control are not only less efficient, but also more expensive.

Table 2.4. Costs of five types of control equipment for primary aluminium smelters

| Control Type | Capital cost * | Annual capital charge + | Operating cost + | Recovery credit + | Total annual cost + |
|---|---|---|---|---|---|
| Tall stack | 50 | 8.85 | 3.04 | 1.72 | 10.17 |
| Wet secondary only | 110 | 19.40 | 7.97 | - | 27.37 |
| Wet primary | 108 | 19.20 | 14.30 | 8.50 | 25.00 |
| Dry primary | 75 | 13.30 | 11.20 | 10.50 | 14.00 |
| Primary + wet secondary | 174 | 30.80 | 17.20 | 11.80 | 36.20 |

* Dollars per metric ton of annual production capacity.
\+ Dollars per metric ton of aluminium produced.

Source: IPAI Report, op.cit.

## 2.4 Emission standards

The main pollutants from an aluminium production plant are fluorine and $SO_2$. Emission standards have been set in most industrialized countries. In 1976 the United States Environmental Protection Agency (EPA) published standards of performance to be applied to any new electrolysis plant, which limits the total fluorine emission to 0.95 kg per ton of Al produced. For the bake oven the limit is 0.05 kg so that the total is 1 kg of F per ton of Al. These limits are observed in several countries.

In addition, emission concentrations are set. For example the State of Washington (USA) imposes that F emissions be less than:[11]

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10/ Rush, Russell and Ireson, "Air Pollution on Primary Aluminium Potlines: Effectiveness and Cost", Journal of the Air Pollution Control Association, February 1973, Vol. 23, No. 2.

11/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981.

3.68 microg/$m^3$ over 12 hours

2.86 microg/$m^3$ over 24 hours

1.64 microg/$m^3$ over 1 week

0.82 microg/$m^3$ over 1 month

0.50 microg/$m^3$ over from 1 March until 31 October

Similar standards are also enforced in countries such as the Federal Republic of Germany and Japan. Fluorine emissions from the plant do not usually cause any harm to the population since no fluorosis (a skeletal disorder caused by fluorine intake) has been observed in the vicinity of modern aluminium plants.

As for $SO_2$, the United States standards are that an industrial plant must not cause an increase in the ambient air concentration in the vicinity of the plant which is in excess of 40 microg/$m^3$ (annual average) or 182 microg/$m^3$ (24 hour average).

Standards are also set for liquid effluents. In the United States the discharge limitations for primary aluminium smelters are:[12/]

Primary aluminum-smelting

| | Maximum 24-hour |
|---|---|
| Fluorides (total) | 0.05 kg/ton aluminium |
| TSS | 0.10 " " |
| pH | 6-9 units " |

Secondary aluminum-smelting

| | Maximum 24-hour |
|---|---|
| Fluorides (total) | 0.4 kg/ton aluminium |
| TSS | 1.5 " " |
| $NH_3$ (as N) | 0.01 " " |
| Al | 1.0 " " |
| Cu | 0.003 " " |
| pH | 6-9 units " |

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12/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984, p. 239.

## 2.5 Health protection for workers

In bauxite ore extraction and subsequent alumina production, potential problems in the working environment result from:

- Operating heavy equipment and machinery,
- Handling corrosive chemicals such as caustic soda and acid, and
- Being exposed to heat, noise, fumes, dusts, welding fumes, and certain toxic chemicals.[13/]

Consequently adequate protection systems and safety regulations must be applied. Most of these potential problems and required practices are not unique to alumina production plants. For aluminium smelters, the exposure of workers to harmful pollutants varies considerably with the different operations that the worker undertakes during his shift. In most industrialized countries health protection standards require that a given time-averaged concentration value of the pollutant not be exceeded during an eight hour working period. Table 2.5 shows typical values pertaining to the most common pollutants found in smelting plants.

However the worker may be exposed to higher pollutant concentrations during certain operations which last only a few minutes. Examples are replacement of anodes in prebake pots or stud removal from Söderberg pots. Peak concentrations can be as high as:[14/]

| | |
|---|---|
| HF | = 20 $mg/m^3$ |
| Fluoride (F) | = 25 $mg/m^3$ |
| CO | = 200 $mg/m^3$ |
| $SO_2$ | = 100 $mg/m^3$ |

Consequently the work area is always ventilated, even in older plants. New plants generally have a system for distributing the ventilation air from the plant floor so that the worker is situated in a rising flow of clean air. Additional improvements to limit the concentration of pollutants in the work area are:

(a) Reduction of the sulphur content of the anode coke with consequent reduction of the amount of $SO_2$ generated;

(b) Increased hood collection efficiency;

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13/ "Guidelines for the Environmental Management of Alumina Production", UNEP, Industry and Environment Guidelines Series.

14/ "Environmental Aspects of Aluminium Smelting", UNEP, Industry and Environment Technical Review Series, Vol. 3, 1981, p. 29.

(c) Reduction of the $SO_2$ adsorption efficiency of the dry alumina process.[15] This is the most effective measure since most of the $SO_2$ escapes through the stack.

(d) Collection of skirt fumes by placing panels above the skirt to form a sort of hood in Söderberg pots.[16]

Another possible harmful effect is caused by noise. In a smelter there are many situations where the NIOSH organization (USA) limit of 90 dB is exceeded (e.g. coke or pitch grinding, forming of prebaked anodes, crust breaking, metal tapping by vacuum siphon). This nuisance factor can be reduced in several ways, such as encasing the equipment in noise-absorbing porous materials.[17][18]

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15/ Alcan, W.D. Lamb, The Role and Fate of $SO_2$ in the Aluminium Reduction Cell Dry Scrubbing Systems, AIME 1979.

16/ UNEP/UNIDO, "Record of the Workshop on the Environmental Aspects of Alumina Production", Paris, (UNEP/WS/Al.7 Final), 1981.

17/ Intalco Aluminum Corporation, K.G. Sandell, Noise Control in an Aluminum Reduction Plant, AIME 1974.

18/ Swiss Aluminium, W. Schmidt-Hatting, Investigations of Noise in Aluminium Electrolysis Cells, AIME 1975.

Table 2.5. Threshold Limit Values (TLV) concerning health protection of workers

| | |
|---|---|
| **A. Fluoride (USA, NIOSH)** | |
| HF as F | 2 mg/m$^3$ |
| Particulate fluorides as F | 2.5 mg/m$^3$ |
| Total HF as F and particulate fluorides as F | 2.5 mg/m$^3$ |
| $F^-$ in urine* | 4 mg/l preshift after 48 h. of non-exposure<br>7 mg/l postshift taken on 4th or later day of the workweek |

*Not an official TLV, but applied at all smelters. Both of these values of 4 mg/l and 7 mg/l are applicable to work groups (e.g. anode changer) and the number represents geometric mean values for each of these individual job groups.

| | |
|---|---|
| **B. Other contaminants (USA)** | |
| $SO_2$ | 5 mg/m$^3$ |
| Total suspended particulates | 10 mg/m$^3$ (respirable 5 mg/m$^3$) |

| | |
|---|---|
| **C. Coaltar pitch volatiles (USA)** | |
| Benzene soluble organics | 0.2 mg/m$^3$ |

This TLV is still applied, but research has shown that the dangerous Particulate Aromatic Hydrocarbons (PAH) are found in varying concentrations. Research is under way to develop a simple chromatographic method which would allow several specific PAH's to be measured.

There is a tendency to replace benzene by the less toxic cyclohexane as solvent.

| | |
|---|---|
| **D. Polycyclic aromatic hydrocarbons** (thin layer chromatography) | |
| Norway - Total PAH | 40 microg/m$^3$ |
| Sweden - Benzo-3, 4-Pyren alone | 5 microg/m$^3$ |

Source: "Guidelines for Environmental Management of Aluminum Smelters", UNEP, Industry and Environment Guidelines Series, 1986, p. 37.

# 3. NICKEL

## 3.1 Pollution control technologies for sulphide ore processing plants

Water is used in mines to dampen the ore. This method plus adequate forced ventilation limits the concentration of airborne dust to some 1 mg/m$^3$. Water must be treated before being discharged from mines and tailings areas at central wastewater facilities. Usually the stream is neutralized to pH 9 to precipitate the heavy metals. Flocculation and clarification is then applied, providing good quality water, acceptable for discharge.

Table 3.1. Concentrations of airborne nickel in some hydrometallurgical operations

| Operation | Number of samples | Range of concentrations (mg Ni/m$^3$) | Average concentration (mg Ni/m$^3$) |
|---|---|---|---|
| Acid leach of matte | - | 0.005-1.630 | 0.099 |
| Purification of nickel electrolyte: | | | |
| Tube filterman | 12 | 0.013-0.316 | 0.144 |
| | | 0.011-0.316[a] | 0.129 |
| Filter pressman | 16 | 0.061-0.535 | 0.209 |
| | | 0.031-0.246[a] | 0.152 |
| Filter-press area | 11 | 0.064-0.508 | 0.242 |
| | | 0.052-0.466[a] | 0.221 |
| Purification of nickel electrolyte (area samples) | | | |
| Cementation of copper on nickel in Pachuca tanks | 39 | 0.048-0.644 | 0.168 |
| | | 0.001-0.133[a] | 0.038 |
| Removing iron slimes with a tube filter | 56 | 0.027-0.653 | 0.200 |
| | | 0.003-0.433[a] | 0.085 |
| Oxidizing cobalt with chlorine | 47 | 0.030-0.672 | 0.183 |
| | | 0.001-0.267[a] | 0.066 |

[a] Soluble nickel

Source: Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

In addition, water is recycled (as much as 85 per cent at some facilities). Improved concentration yields during the ore concentration step have been proven to be very beneficial to both the nickel industry and the environment. For example, at the Inco facility in Sudbury the nickel concentrate stream used to contain 4 per cent nickel and 60 per cent nickel ferrous pyrrotite. This meant that for each ton of nickel produced 26 tons of concentrate were processed, 17 tons of iron sulfide were burnt producing 13 tons of $SO_2$ and 26 tons of slag. Currently for each ton of nickel produced the corresponding figures are respectively 10, 6, 4.3 and 10 tons.

The problem of tailings disposal has been partially circumvented by mine backfilling with the coarser fraction of the tailings. Some 20 per cent of the tailings is so disposed of at some locations. Still the problem remains for the finer fraction of the tailings which tends to create dust. A method which has been used to control the situation is that of wetting the disposal area followed by its revegatation. At the Sudbury facility this method has been employed since the mid 1950's for tailings basins.[19/20/] Grass species (e.g. timothy), legumes (alfalfa), and trees (birch, willow) were successfully utilized at the INCO area at Copper Cliff.[21/] The environmental advantages are self-evident. In addition, the vegetation can reduce rainfall seepage through the ground and decrease ground moisture content, by transpiration. This, in turn, reduces the chance of tailings leaching into the ground.

Removal of other pollutants such as thiosulphates and polythionates which are formed in the water used in ore processing has been successfully accomplished by proper impoundment, and subsequent oxidation to sulphuric acid by bacteria and sunlight. The acid can then be neutralized with lime.

Fine dusts are produced during many steps in the pyrometallurgical and refining operations (e.g. in roasters, reverberatory furnaces, electric furnaces, converters). These dusts may contain as much as 5-10 per cent nickel and 10-20 per cent sulphate. This problem is usually tackled by improving the hood collection efficiency followed by dust removal with several devices (such as electrostatic precipitator or scrubbing systems) which are described in other chapters.

The problem of $SO_2$ generation is most likely the most serious. Two approaches are possible based on collection of $SO_2$ from flue gases followed by its conversion to other chemical species. The first consists of the conversion of $SO_2$ to marketable chemicals such as elemental sulphur, liquid sulphur dioxide, ammonium sulphate or sulphuric acid. This method should be used whenever economically feasible. In alternative $SO_2$ can be converted to

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19/ Young, C.A. and T.H. Peters, The Use of Vegetation to Stabilize Mine Tailings at Copper Cliff, 68-77. Proceedings of the 15th Ontario Industrial Waste Conference, June 1968.

20/ Michelutti, R., "How to Establish Vegetation on High Iron-Sulphur Mine Tailings", Canadian Mining Journal, October 1974. pp. 54-58.

21/ Peters, T.H., Inco Metals reclamation program, The Canadian Mining and Metallurgical Bulletin, December 1978.

chemicals such as gypsum, and then be disposed of. The gypsum is not saleable due to contamination by heavy metals. This method is not currently used.[22/23/]

3.2 Retrofitting of existing plants to reduce pollution

Improvement of emission quality can be obtained by either altering the process to reduce primary pollutant production (as carried out by INCO at its Sudbury and Thompson plants) or cleaning the off-streams leaving the plant. Improved end-of-the-pipe treatments means improved dust removal efficiency from gases, and $SO_2$ emission control. Whenever feasible dry systems are be preferred for dust removal. Wet scrubbers may result in polluted wastewater streams. If not presently fitted, a cyclone should be retrofitted to all dust laden streams in old plants. Electrostatic precipitators offer higher removal efficiencies, especially for finer particles, but are more expensive.

Removal of $SO_2$ from flue gas is possible through the contact sulphuric acid production process, the chemical absorption process, or the elemental sulphur production process. Existing large nickel production facilities are not readily amenable to the introduction of simple $SO_2$ removal processes, especially if $SO_2$ emissions concentrations are low. In contrast, new plants have been built which include facilities for the recovery of as much as 80 per cent of the $SO_2$ generated.

3.3 Pollution control costs

$SO_2$ emissions are the most difficult and the most expensive to control. Several control systems exist, but each is tailored to a type of emisson. The characteristics of the gas streams which are suitable for treatment are reported in table 3.2[24/] for each of the most common removal systems. No economic process is currently available for treating low $SO_2$-content gases, although studies are underway.

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22/ "Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters", EPA-450/2-74-002 a.

23/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-3, April 1980.

24/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-8, April 1980.

Table 3.2. Characteristics of gas streams required for optimum treatment in sulphur recovery plants

| | Percentage $SO_2$ | Percentage $O_2$ | Flowrate and composition |
|---|---|---|---|
| Contact acid - single | 5-8 | 8-12 | Can be variable[1] |
| - double | 5-8 | 8-12 | Can be variable[1] |
| Liquid $SO_2$ - physical | 70-80 | Low as possible | Constant |
| - chemical | 10-11[2] | - | Constant |
| Elemental sulphur | 10 | 1-3 | Constant |

1. More economical when constant.

2. Plant requires pressure or chemical absorption followed by treatment of strong regenerated stream.

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

In addition to the cost for $SO_2$ removal from off-gases, considerable costs are associated with by-product manufacture (such as sulphuric acid, liquid $SO_2$, elemental sulphur), marketing, transportation, storage or final disposal. For example, 300 Km is considered to be the maximum distance for economically shipping sulphuric acid.[25/] By contrast, most nickel plants are located far away from potential markets.

The ratio of sulphur to nickel in concentrates usually varies between 2.2-4.8 and can greatly affect $SO_2$ control cost. Table 3.3[26/] presents such cost for different fixation systems assuming that the final product had no value.

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25/ Anon., New Smelter, Acid Plant at Falconbridge to Improve Working Conditions, Efficiency, Canadian Mining Journal, 99, 5, May 1978.

26/ Environment Canada, A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industry, Report EPS 3-AP-79-8, April 1980.

Table 3.3. Cost of sulphur fixation per pound of nickel produced*

| | Single catalysis acid plant | | | | | | Double catalysis | |
|---|---|---|---|---|---|---|---|---|
| | Continuous gases only | | Variable gases only | | Continuous and variable gases | | Continuous and variable gases | |
| Sulphur fixation, percentage | 50 | 45 | 95 | 97 | | | | |
| Production cost $US/ton S | 59 | 92 | 54 | 58 | | | | |
| Neutralization cost $US/ton S | 92 | 92 | 86 | 86 | | | | |
| Sulphur/metal ratio in concentrate | Low | High | Low | High | Low | High | Low | High |
| Sulphur fixation costs cents/lb Ni | 2.95 | 6.43 | 4.14 | 9.02 | 5.12 | 11.18 | 5.64 | 12.31 |
| Neutralization (total cost of making acid and neutralizing it) cents/lb Ni | 7.57 | 16.51 | 8.29 | 18.09 | 13.25 | 28.91 | 13.94 | 30.42 |

* Gas cleaning costs not included

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

## 3.4 Emission standards

Emission standards for $SO_2$, the major pollutant, can be found in other chapters (Aluminum, Copper). Emission level for particulates in the air should be maintained below 240 micrograms/$m^3$ over a 24-hour emission peak, and below 75 micrograms/$m^3$ as annual geometrical mean.[27/] The maximum airborne nickel concentration must be below 20 mg/$m^3$. Concentration of nickel exceeding 50 mg/kg can be toxic to plants. Therefore, the amount of

27/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

nickel salts dispersed on land used for agricultural purposes should be limited, particularly on acid soils. The UK Department of the Environment recommends that not more than 7 $g/m^2$ (as Ni) should be added to the soil over a period of 30 years.[28] As for liquid effluents from nickel plants, when impoundment is not feasible, the Canadian authorities recommend the following limits:

| | |
|---|---|
| Total Suspended Solids | 15 mg/l (30-day average) |
| Cu | 0.2 " |
| Ni | 0.5 " |
| Fe | 0.5 " |
| pH | 6-9 units |

## 3.5 Health protection for workers

Occupational exposure limits for airborne nickel in working environments have been adopted by several countries and are reported in table 3.4.

Table 3.4. Maximum occupational exposure limits for airborne nickel

| | | | | | USA | | |
|---|---|---|---|---|---|---|---|
| | | | | | | ACGIH | |
| | Fed. Rep. Germany | Japan | Sweden | USSR | Occup. standard | TWA | Short term |
| Nickel, $mg/m^3$ | | 1 | 0.01 | 0.5 | 1 | 1 | |
| Nickel carbonyl, $mg/m^3$ | 0.7 | 0.007 | 0.007 | 0.0005 | 0.007 | 0.35 | 0.35 |

Source: Occupational Exposure Limits for Airborne Toxic Substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

28/ "Environmental Aspects of Selected Non-Ferrous Metals Industries", UNEP, Industry and Environment Overview Series, 1984.

As an example of actual worker exposure table 3.5[29/] shows data made available by Société Métallurgique Le Nickel for its plant in New Caledonia. The data presented indicate that airborne nickel concentrations are quite low although this may be due largely to the low nickel content of the ore.

Table 3.5. Concentrations of airborne nickel in laterite mining and smelting: New Caledonia

| Concentration of airborne nickel (mg Ni/m$^3$) | Area sampling | | Personal sampling | |
|---|---|---|---|---|
| | Frequency of observation (per cent) | Average concentration[a/] | Frequency of observation (per cent) | Average concentration[a/] |
| 0.05 | 67.1 | 0.0047 | 83.2 | 0.0022 |
| 0.05-0.10 | 8.3 | 0.076 | 1.4 | 0.081 |
| 0.10-1.00 | 24.6 | 0.029 | 15.5 | 0.274 |

[a/] Sampled for particles less than 30 microns in diameter.

Source: Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

In general the hazard to workers depends strongly on the nickel compound involved. Whereas nickel metal and most of its inorganic salts are relatively non-toxic, nickel carbonyl gas (present in some refining processes) is toxic even at low concentrations. Consequently workers must be adequately protected from it. Moreover, experimental studies have concluded that several nickel compounds can produce malignant tumors in animals if inhaled (nickel subsulphate and carbonyl) or injected (nickel subsulphide, oxide, carbonate, hydroxide).[30/] Indeed there is now substantial evidence to state that

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29/ Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

30/ Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol. II., International Agency for Research on Cancer, Lyon, 1976. pp. 75-112.

workers in nickel refineries run some risk of nasal and pulmonary cancer. The data came from refineries in Canada, Japan, Norway, GDR, and USSR. Although no conclusive evidence has been found it appears that inhaled dust particles of nickel oxide and nickel carbonyl vapors can be held responsible.[31/32/] The analysis of the data also shows that the risk of refinery workers to develop cancer has significantly decreased over time, probably as a consequence of the improved working conditions. Some estimates of the concentrations of airborne nickel in some refining operations where there was in the past an increased incidence of cancer were from one to two orders of magnitude higher than those found in the nickel industry today.

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31/ IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Chemicals and Industrial Processes Associated with Cancer in Humans, IARC Monographs Volumes 1-20, IARC Monographs Supplement 1, International Agency for Research on Cancer, Lyon, September 1979.

32/ Warner, J.S., "Occupational Exposure to Airborne Nickel in Producing and Using Nickel Products", in "Nickel in the Human Environment", International Agency for Research on Cancer, Oxford University Press, 1984.

# 4. COPPER

## 4.1 Pollution control technologies for copper production plants

### 4.1.1 Pollution control during mining

Dust is the main environmental problem at this stage. Dust generated by truck hauling can be reduced by employing trucks of greater capacity and covering the roads with a non-dusty upper layer. Emulsions can be used for this purpose. Additional advantages of this method are increases in both haulage speed and tire life by 10-15 per cent.[33/] The amount of dust produced by blasting can be reduced by spraying a solution of calcium hydroxide or sodium sulphate (10 per cent) in blast holes. Dust formation at open pit mining sites can be reduced by creating a light mist with steam-air jets. Reforestation is important for both land reclamation and to create green buffer areas to prevent dust and harmful chemicals from spreading. One hectare of forest may collect up to 18 tons of dust. Sowing of perennial cereals can be used to eliminate dust formation at spent open pit mining sites.

### 4.1.2 Pollution control during ore processing

Dust is again the main environmental problem. During crushing and grinding the most effective method to prevent dust formation is to sprinkle or spray water. In a closed room it is necessary to seal the dust generating equipment, provide good ventilation, and use dust collecting equipment. Dust collection efficiency at this stage can be as high as 95 per cent. Remote control of these operations is the rule.

The main environmental problem of ore flotation is water pollution caused by floating agents. This has been partially circumvented in recent years by replacing highly toxic cyanide salts with sulphides, and toxic phenolic foaming agents of the cresol type with non-phenolic agents. In addition, water recycling has been extensively introduced.

### 4.1.3 Pollution control during ore concentrate roasting

This operation can be the highest single-step desulphurization of the whole copper production process (50-70 per cent removal). Fluidized bed roasting produces $SO_2$ in concentrations high enough (up to 14 per cent) to allow high recovery rates (up to 99.5 per cent). This increases the overall sulphur recovery efficiency of the whole production process to some 75-85 per cent. Other low-$SO_2$ content streams generated by other operations can be diluted with the roaster off-gas stream. The resulting stream can still be efficiently processed (e.g. in a $H_2SO_4$ plant) for $SO_2$ removal. However, in multiple hearth furnaces the $SO_2$ content in the off-gas is only 7.5 per cent. This is still suitable for efficient $SO_2$ removal, but not for dilution with other gas streams. Roasting gases also contain dust which is usually removed in cyclones and electrostatic precipitators.

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33/ "Environmental Aspects of Copper Production", UNEP Workshop, Geneva, 13-16 April 1981.

4.1.4 Pollution control during matte production

If reverberatory furnaces are used as smelters, off-gases have an $SO_2$ content which is too low for effective removal. Consequently no control exists at present. Waste heat recovery is practiced, then dust is removed from the off-gases in electrostatic precipitators (efficiency higher than 99 per cent). The collected dust is then recycled.

If blast smelting is adopted the roasting step is replaced by a pelletizing-sintering step which generates a gas stream whose $SO_2$ content (about 7 per cent) is suitable for conversion to sulphuric acid. If the modified pyritic process follows $SO_2$ can still be removed from the gas stream although less efficiently. With the semi-pyritic blast smelting this is no longer possible since $SO_2$ content is too low (below 2 per cent).

In electric smelting, the concentration of $SO_2$ in the off-gases is very high. No air is admitted to the smelter (provided proper sealing exists, mainly near the electrodes), and the gas volume is low. The dust content is also low and this allows the use of smaller electrostatic precipitators.

Flash smelting also produces off-gases with high $SO_2$ content (up to 30 per cent) which may become even higher if nearly pure oxygen is used (85-95 per cent). These gases can be diluted with other streams from other parts of the plant and are suitable for very efficient sulphur removal.

4.1.5 Pollution control during matte conversion

Beside $SO_2$ and dust, fume leakage is the main environmental problem. This can be effectively circumvented by proper hood design, operation, and maintainance. $SO_2$ concentrations in off-gas average 4-4.8 per cent and sometimes even higher values (provided some measures are taken, such as effective hood and gas duct sealing, hood water and evaporation cooling). These lower concentrations limit the $SO_2$ recovery efficiency to about 50 per cent (sometimes values up to 85 per cent can be obtained), in a sulphuric acid production plant.

4.1.6 Pollution control during fire refining

The furnace produces off-gases having an $SO_2$ content less than 0.3, which is too low for removal. Waste heat boilers may be fitted to the furnace for waste heat recovery and dust trapping. The gas is then released into the atmosphere without any further treatment because of its low content of pollutants. Sometimes further dust removal could still constitute a good practice.

4.1.7 Pollution control during electrorefining

Shop ventilation air is usually vented without treatment. As for waste water, its heavy metal content is removed by neutralization with lime, which precipitates the metals as salts. More advanced methods such as ion exchange or flocculation can also be employed.

4.1.8 Pollution control for hydrometallurgical processes

In hydrometallurgy liquids and sludges require disposal. There is also a potential for acid seepage. Whereas pyrometallurgical slags are solid and

inert, hydrometallurgical sludges may contain undissolved metals, acid, and large quantities of water. They are usually impounded in ponds, which must be water proofed.

4.1.9 Removal of sulphur dioxide from gas streams

Sulphur dioxide is present in all gaseous streams produced by smelters in concentrations ranging between 0.1 and 95 per cent. At present, industrial technologies exist to remove $SO_2$ provided that its concentration is above 4 per cent. Recovery of $SO_2$ and its subsequent conversion to $H_2SO_4$ not only eliminates the associated pollution problems, but also may improve the overall economies of the copper manufacturing process. Technologies exist also for streams with lower $SO_2$ concentrations, but they are not industrially used because of their cost. $SO_2$ can be converted to sulphuric acid, elemental sulphur, liquid sulphur dioxide, ammonium sulphate or gypsum. Table 4.1 shows the concentration requirements for the stream to be purified for each method.[34/]

Table 4.1. Characteristics of gas streams required for optimum treatment in sulphur recovery plants

| | | Percentage $SO_2$ | Percentage $O_2$ | Flowrate and composition |
|---|---|---|---|---|
| Contact acid | - single | 5-8 | 8-12 | Can be variable[a/] |
| | - double | 5-8 | 8-12 | Can be variable[a/] |
| Liquid $SO_2$ | - physical | 70-80 | Low as possible | Constant |
| | - chemical | 10-11[b/] | 0 | Constant |
| Elemental sulphur | | 10 | 1-3 | Constant |

a/ More economical when constant.
b/ Plant requires pressure or chemical absorption followed by treatment of strong regenerated stream.

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April, 1981.

Contact sulphuric acid process

This is the most common method for recovering $SO_2$. The process consists of contacting $SO_2$ and oxygen in the presence of a catalyst (vanadium pentoxide) to form $SO_3$, which is then converted to $H_2SO_4$ by

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34/ Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April 1981.

adding water. The reaction is exothermic and heat can be recovered. The process operates with $SO_2$ concentrations between 5 and 8 per cent and oxygen concentrations from 30-50 per cent higher than the $SO_2$ concentration. The conversion efficiency is 97 per cent and 99.5 per cent for single and double contact plants respectively. A major economic drawback is that the acid must be transported to the market places which are usually far away from the production point.

Elemental sulphur processes

Several processes have been developed (Outokumpu Allied Chemical, ASARCO, Texagulf). They are all based on a two step process consisting of reducing the $SO_2$ to $H_2S$ and then catalytically converting the hydrogen sulphide to sulphur, recycling the reactant. Only concentrated $SO_2$ streams (10-15 per cent) can be processed. The oxygen content must be rather low (below 3 per cent). The conversion efficiency is about 90 per cent. The main advantage of the process is that sulphur is easy to transport and store.

Liquid sulphur dioxide process

This process can operate only with an $SO_2$ concentration as high as 70-80 per cent and practically no oxygen. The off-gas must be clean. It is compressed and refrigerated until $SO_2$ liquifies. Alternatively, $SO_2$ can be removed from the original gas stream by absorption and subsequent regeneration in concentrated form, and then liquefied.

## 4.2 Retrofitting of existing plants to reduce pollution

In recent years major emphasis has been placed on increasing the efficiency of ore processing. In order to reduce energy consumption some plants have been retrofitted with systems capable of grinding the ore to a much finer product so that mineral recovery is enhanced. Process control has been upgraded by introducing on-stream analysis methods and automated control loops.

A promising technology to enhance flotation efficiency is the reverse flotation process. The gangue is floated rather than the copper-rich ore. This system has already been used at the CRA company's Woodlawn mine in Australia.[35/]

As for smelting operations, the main environmental problem in old plants is the emission of $SO_2$. More often than not, $SO_2$ content in off-gases (especially from reverberatory furnaces or converters) is too low for removal. In principle, it is technically feasible to reduce such emissions to very low level. For example, low-concentration $SO_2$ in the off-gas could be absorbed and then released to give a more concentrated stream. In practice this technology is not yet economical. Therefore most old smelters keep

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35/ "Impact of New Technologies on the World Copper Market - A Study Prepared for UNCTAD", Commodities Research Unit Ltd. (London) and CRU Consultants Inc. (New York), 1986.

releasing untreated $SO_2$. In order to minimize adverse effects on life and the environment in the neighborhood of the plant, a tall stack could be provided for efficient dispersion into the atmosphere. However long range transport of $SO_2$ has already caused acid rain in northern Europe and North America.

A more satisfactory approach consists of retrofitting old converters with oxygen-enriched air blowing systems. This results in a more energy efficient process which also means that smaller amounts of gases are produced, and $SO_2$ is more concentrated. An example of such a system comes from the "Teniente Modified Converter" developed by Codelco for smelting El Teniente ore concentrates (Chile). Here the basic configuration of the existing smelter was modified and oxygen-enriched fuel burners were introduced on the roof of the converter. This resulted in an increased production of 600 tons/day of copper without any additional fuel consumption, in a single smelting-converting operation. Converters with side removal of gases can have similar advantages. These systems give higher copper and $SO_2$ recovery efficiency with limited capital investment for modernization.

Retrofitting is possible in hydrometallurgy due to the adoption of new solvents. After leaching the copper from the ore with a sulphuric acid solution, this stream is contacted with an organic solution to recover copper. The most common reagent used during this solvent extraction step is General Mills' LIX 64 (Liquid Ion Exchange). This solvent (of proprietary composition) selectively reacts with copper. Since then the development of second generation reagents such as LIX 860 has enabled existing plants to reduce operating costs and increase recovery efficiency. The newest reagents are not too sensitive to pH variations and can therefore operate at higher loading capacity using more acidic copper solutions.

4.3 Pollution control costs

For a new reverberatory furnace (1,500 tons/day capacity) the smelting cost can be estimated to be 97.8 cents/kg of copper produced.[36] This cost does not include $SO_2$ emission control or particulate matter recovery costs. On the other hand the smelting cost for a new flash smelter is only 61 cents/kg[37] and this figure includes the cost for complying with existing air emission standards.

For those cases where $SO_2$ can be effectively removed from the off-gases (i.e. where $SO_2$ concentration is high enough) an estimate of the removal cost is given in table 4.2[38] for different methods. The table shows

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36/ "Compendium of Low- and Non- Waste Technology", Copper Production Using the Noranda Process, UN Economic and Social Council, 1 May 1984.

37/ "Compendium on Low-and Non- Waste Technology", Primary Copper Production Using the Outokumpu Flash Furnace, UN Economic and Social Council, 1 May 1984.

38/ "Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters", EPA-450/2-74-002 a.

only order of magnitude costs and does not include hot gas cleaning systems (which could increase the cost by as much as 30 per cent). No modifications of or adaptations to the existing plant were considered.

Table 4.2. Cost of sulphur fixation per pound of copper produced*

| | Single catalysis acid plant | | | | | | Double catalysis | |
|---|---|---|---|---|---|---|---|---|
| | Continuous gases only | | Variable gases only | | Continuous and variable gases | | Continuous and variable gases | |
| Sulphur fixation, percentage | 50 | 45 | 95 | 97 | | | | |
| Production cost $US/ton S | 59 | 92 | 54 | 58 | | | | |
| Neutralization cost $US/ton S | 92 | 92 | 86 | 86 | | | | |
| Sulphur/metal ratio in concentrate | Low | High | Low | High | Low | High | Low | High |
| Sulphur fixation costs cents/lb Cu | 1.07 | 2.14 | 1.50 | 3.01 | 1.86 | 3.73 | 2.05 | 4.10 |
| Neutralization (total cost of making acid and neutralizing it) cents/lb Cu | 2.75 | 5.50 | 3.02 | 6.03 | 4.67 | 9.64 | 5.07 | 10.14 |

(Canada - 1979)

* Gas cleaning costs not included

Source: Lemmon, W.A., "Environmental Aspects of the Extraction and Production of Nickel", UNEP Workshop, Geneva, 13-16 April, 1981.

As for dust removal an idea of the costs associated with different technologies and removal efficiencies can be obtained from table 4.5.[39/] Cost figures are from 1972.

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39/ Stone, E.H.F., "Fume and Effluent Treatment Plant in the Non-Ferrous Metals Industry", Institute of Metals, Review 169, 1972.

Table 4.3. Efficiency and cost of control equipment for 1,000,000 $m^3/h$ dusty gases at 20°C

| Equipment | Removal efficiency, standard dust (%) | Total running cost (£ per annum) | Total cost including capital charges (£ per annum) |
|---|---|---|---|
| Inertial collector | 58.6 | 587 | 1,313 |
| Medium-efficiency cyclone | 65.3 | 1,233 | 1,693 |
| Low-resistance cellular cyclone | 74.2 | 480 | 1,380 |
| High-efficiency cyclone | 84.2 | 1,547 | 2,567 |
| Tubular cyclone | 93.8 | 1,360 | 2,467 |
| Electrostatic precipitator | 99.0 | 933 | 5,867 |
| Shaker-type fabric filter | 99.7 | 3,380 | 6,847 |
| Low-velocity fabric filter | 99.8 | 3,127 | 6,327 |
| Reverse-jet fabric filter | 99.8 | 6,640 | 11,507 |
| Jet-impingement scrubber | 97.9 | 2,807 | 4,807 |
| Irrigated cyclone | 91.0 | 1,900 | 3,153 |
| Self-induced spray deduster | 93.6 | 2,093 | 3,493 |
| Spray tower | 94.5 | 4,000 | 6,933 |
| Fluidized-bed scrubber | 95.0 | 3,067 | 4,180 |
| Irrigated-target scrubber | 97.9 | 2,513 | 4,247 |
| Disintegrator | 98.5 | 15,840 | 18,707 |
| Irrigated electrostatic precipitator | 99.0 | 1,320 | 7,653 |
| Low-energy annular-throat scrubber | 99.5 | 4,933 | 7,067 |
| Medium-energy Venturi scrubber | 99.7 | 7,293 | 9,560 |
| Medium-energy annular-throat scrubber | 99.8 | 7,466 | 9,733 |
| High-energy Venturi scrubber | 99.9 | 10,933 | 13,400 |

Source: E.H.F. Stone, op.cit.

4.4 Emission standards

According to The World Bank emission levels in off-gases should be maintained below the following figures:

Table 4.4. World Bank guidelines for emission levels in off-gases

| | | | |
|---|---|---|---|
| Sulfur dioxide ($SO_2$) | | | |
| Inside plant fence | Annual arithmetic mean | 100 | $g/m^3$ |
| | Maximum 24-hour peak | 1,000 | $g/m^3$ |
| Outside plant fence | Annual arithmetic mean | 100 | $g/m^3$ |
| | Maximum 24-hour peak | 500 | $g/m^3$ |
| Particulates | | | |
| | Annual geometric mean | 75 | $g/m^3$ |
| | Maximum 24-hour peak | 260 | $g/m^3$ |
| Nitrogen oxides (as $NO_2$) | | | |
| | Annual arithmetic mean | 100 | $g/m^3$ |
| Carbon monoxide (CO) | | | |
| | Maximum 8-hour average | 10 | $mg/m^3$ |
| | Maximum 1-hour average | 40 | $mg/m^3$ |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

The UK emission standards for the off-gases emitted by copper production plants have the following values: total particulates shall not exceed 0.46 $g/m^3$ for emission up to 700 $m^3$/min reducing to 0.23 $g/m^3$ for larger emissions. Copper and zinc shall not exceed the limit of 0.115 $g/m^3$. Other standards are set for cadmium and lead, depending on the size of the plant. For large emissions the limits are 0.012 $g/m^3$ and 0.7 kg/hr for cadmium, and 0.012 $g/m^3$ and 5.4 kg/hr for copper. The minimum stack height is fixed at 30 meters.[40/]

For liquid effluents different standards are applicable to different plants.

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40/ Butler, D.H., "Copper, Environmental Impact in Its Processing, Use and Disposal", UNEP, Industry and Environment Programme, Paris, 1 September 1982.

Table 4.5. Standards for liquid effluents

For primary copper smelting plants the limits are:
(mg/liter of effluent)

| | Maximum 24-hour | Consecutive 30-day average |
|---|---|---|
| TSS | 50 | 25 |
| As | 20 | 10 |
| Cu | 0.5 | 0.25 |
| Pb | 1.0 | 0.5 |
| Cd | 1.0 | 0.5 |
| Se | 10 | 5 |
| Zn | 10 | 5 |
| pH | 6-9 units | 6-9 units |

For electrolytic copper refining plants the limits are:
(kg/metric ton of product)

| | Maximum 24-hour | Consecutive 30-day average |
|---|---|---|
| TSS | 0.10 | 0.05 |
| Cu | $1.7 \times 10^{-3}$ | $0.8 \times 10^{-3}$ |
| Cd | $6 \times 10^{-5}$ | $3 \times 10^{-5}$ |
| Pb | $6 \times 10^{-4}$ | $2.6 \times 10^{-4}$ |
| Zn | $1.2 \times 10^{-3}$ | $0.3 \times 10^{-3}$ |

For secondary copper refining plants the limits are:
(mg/liter of effluent)

| | Maximum 24-hour | Consecutive 30-day average |
|---|---|---|
| TSS | 50 | 25 |
| Cu | 0.5 | 0.5 |
| Zn | 10 | 5 |
| Oil and Grease | 20 | 10 |
| pH | 6-9 units | 6-9 units |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

## 4.5 Health protection for workers

Copper is a metal of fairly low toxicity. The paucity of literature on ill effects caused by exposure to it seems to confirm this.[41/42/] Some occupational exposure limits for airborne copper, as recommended in selected countries, are reported in table 4.6.[43/]

Table 4.6. Occupational exposure limits for airborne toxic substances

| | | | | | USA | | |
|---|---|---|---|---|---|---|---|
| | | | | | | ACGIH | |
| | Fed. Rep. Germany | Japan | Sweden | USSR | Occupat. stand. | TWA | Short term |
| Copper dust mg/m³ | 1 | | 1 | 1 | 1 | 1 | 2 |
| Copper fumes mg/m³ | 0.1 | | | | 0.1 | 0.2 | 0.2 |

Source: ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

Copper melts and boils at relatively high temperatures. Consequently it does not release metal fumes as readily as other metals such as lead, cadmium or zinc. Furthermore, copper dust and fumes have a characteristic odor which gives a warning to the workers, thus limiting exposure before toxic intake can occur. Nevertheless workers can develop undesirable health effects if limit concentrations are exceeded. In extreme cases, metal fume fever, a 24-48 hour illness can result. Contact dermatitis has also been reported,[44/] but observations of copper smelter and refinery workers over more than 25 years have failed to show any significant incidence of dermatitis. In copper smelting operations it is likely that more harmful metal fumes will be present

41/ "Copper, Medical and Biological Effects of Environmental Pollutants", The National Research Council, National Academy of Sciences, Washington, D.C., 1977.

42/ Demayo, A., M.C. Taylor, and K.W. Taylor, "Effects of Copper on Humans, Laboratory and Farm Animals, Terrestrial Plants, and Aquatic Life", August 1982.

43/ Nordman, H., UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO UN Environmental Programme.

44/ Saltzer, E.I., and J.W. Wilson, "Allergic Contact Dermatitis Due to Copper", Arch. Derm. 98:375-376, 1968.

from lead, cadmium, antimony, selenium, berillium, and especially arsenic. All the authors who have reported increased incidence of lung cancer among workers in copper smelters have suggested that arsenic trioxide in dust and fumes was the culprit.[45/46/47/48/]

$SO_2$ can also be considered to be a potentially harmful chemical in the working environment. Its detrimental effect on human health appears at concentrations as low as 0.5 $mg/m^3$, although its odor can only be detected at 2.6-3 $mg/m^3$. Substantial irritant effects appear at 20 $mg/m^3$. Other chemicals and substances (such as humidity and dust) appear to have a synergistic effect in combination with $SO_2$.

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45/ Kuratsune, M., S. Tokudome, T. Shirakusa, M. Yoshida, Y. Tokumitsu, T. Hayano, and M. Seita, "Occupational Lung Cancer among Copper Smelters", Int. J. Cancer 13:552-558, 1974.

46/ Lee, A.M. and J.F. Fraumeni, Jr., "Arsenic and Respiratory Cancer in Man: An Occupational Study", J. Nat. Cancer Inst. 42:1045-1052, 1969.

47/ Milham, S., Jr. and T. Strong, "Human Arsenic Exposure in Relation to a Copper Smelter", Environm. Res. 7:176-182, 1974.

48/ Tokudome, S. and M. Kuratsune, "Cohort Study on Mortality from Cancer and Other Causes among Workers at a Metal Refinery", Int. J. Cancer 17:310-317, 1976.

# 5. LEAD

## 5.1 Pollution control technologies for lead production plants

### 5.1.1 Pollution control during mining

Underground mines are always equipped with a ventilation system which must be capable of bringing fresh air from the outside and, at the same time, sufficiently diluting the spent air containing dust and fumes from mining operations. Dust formation may be limited by spraying water on the rocks or ore prior to each operation. Wastewater produced during mining can be processed in a treatment plant to remove at least the suspended solids and partially recycled. In arid regions the paucity of water may exacerbate the problem and a good water management plan is a must. A good example of this is provided by the Mount Isa Mines Ltd. in Australia. Here a complex system for water collection, pumping and distribution exists which supplies water to all individual demand points.[49/] The opposite problem arises in those mines where water is present in rocks and must be pumped away. It is likely that this water will be acidic and contaminated with dissolved metal salts. Therefore water treatment must be provided. Water treatment in such a case consists of a pH adjustment with lime which precipitates the heavy metals. Upon the addition of coagulants a sludge is formed and then collected in thickeners. The thick sludge is then pumped away and disposed of in lagoons.[50/]

### 5.1.2 Pollution control during ore processing

Air pollution during frothing operations is usually negligible. Dust may be a problem during all the remaining operations involving dry solids handling. Dusty solids may be stored in closed or protective structures to prevent blowing off. During transport on trucks or barges the concentrated ore should be covered in order to avoid the same problem. High concentrations of ore dust in the air (up to 100 meters in height) have been measured along the roads where there is a heavy traffic of loaded trucks.[51/] In order to ease the problem the ore may be shipped with a 10-12 per cent moisture content to the smelting plant.[52/]

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49/ "Operations at Mount Isa", Mount Isa Mines Limited Australia, 1977.

50/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA 430/9-73-011, Washington, D.C., October 1973.

51/ Hemphill, D.D., "Lead Contamination Along Roadways", in Lead in the Environment, Boggess, W.R. and Wixon, B.G. (ed.), Natl. Sci. Foundation, NSF/RA-770214, Washington, D.C., 150, 1977.

52/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

Water pollution can be a serious problem because of the presence of flotation agents and tailings. Whenever possible recycling should be adopted. In many mines mine water is used for subsequent operations such as milling and flotation. Waster water slurries containing tailings can be disposed of in three possible ways: underground, in tailings ponds, and in seas. Underground disposal is adopted by many companies. This method consists of pumping the slurry back to the spaces left empty from mining operation, sometimes with the addition of cement. This method has the lowest environmental impact.

Impoundment in tailings ponds creates a potential environmental impact because of possible leaks of contaminated water into the ground. In practice, because of the potential acidic water leakage problem the lead/zinc industry in the USA has been rated second (exceeded only by the uranium industry) in terms of the toxic hazard rating for land disposed wastes.[53/54/] Once the water has evaporated the tailings may be subjected to wind action and dust may be blown off. Consequently the area should be stabilized with some kind of vegetation. In some cases, such as arid regions, where this would be impossible the problem has been overcome by spreading rocks over the dried tailings. This system has been successfully used in Australia.

Marine disposal of tailings is seldom used. However one example is the Greenex Black Angel mine in Greenland. Here the tailings are stabilized with lime and then disposed of in a fjord nearby.[55/]

5.1.3 Pollution control during concentrate smelting

Pollution control during charge preparation

Fugitive dust emissions can be a serious problem because of the high lead content. They can be controlled by wetting the material, or use of effective dust collection devices. Moisture in the charge should never fall below 8 per cent. The collected emissions can be treated in a wet scrubber in order to recover the dust which can then be recycled.

Pollution control during roast sintering

$SO_2$ and dust emissions are the main problems at this stage. Most up-draft sinter machines are capable of producing off-gases with $SO_2$ concentrations of at least 4 per cent, suitable for conversion to $H_2SO_4$ in an acid plant (see chapter on copper for details). This concentration is achieved by recycling gases more dilute in $SO_2$ through the machine until a sufficiently concentrated gas stream is produced.

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53/ "The Health and Environmental Impacts of Lead on an Assessment of a Need for Limitations", Office of Toxic Substances, United States Environmental Protection Agency, EPA-560/2-79-001, Washington, D.C., April 1979.

54/ "Environmental Impacts and Controls in the Extraction and Production of Lead, Zinc and Cadmium", UNEP Workshop, Geneva, 13-16 April 1981.

55/ Greenland Fisheries Investigations, Recipient andersogeke ued Marmorilik, 1980, 1979, 198, 1977, 1976, Ostervaldgade 10, 1350 Kobenhaven, K. Denmark (In Danish with summary in English and Greenlandic).

Off-gases from down-draft machines are too dilute for effective $SO_2$ removal. Consequently they are vented. The off-gases are cooled and processed through bag filters, electrostatic precipitators, or wet scrubbers to collect dust emissions. Cooling condenses the heavy metals. Otherwise condensation of heavy metals can occur within the stack or in the stack plume, with subsequent fallout and environmental pollution. If wet scrubbers are used water will also be contaminated with heavy metals and will require treatment prior to discharge (such as lime addition for heavy metal precipitation). The concentration of the main pollutants in the wastewater stream produced by a smelting plant is given in table 5.1.[56/]

Table 5.1. Pollutant concentration in waste water from lead smelting plant

| | Number of | | Concentration, mg/L | | |
|---|---|---|---|---|---|
| Pollutant | Analyses | Times detected | Range | Median | Mean |
| COD | 3 | 2 | ND* - 170 | 3.7 | 58 |
| TOC | 1 | 1 | | 3.3 | 3.3 |
| TSS | 1 | 1 | | 26 | 26 |
| Total phenol | 2 | 2 | 0.012 - 0.050 | | 0.031 |
| Ammonia | 2 | 2 | 0.43 - 3.8 | | 2.1 |

*ND = not detectable

Source: EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

Pollution control during blast furnace reduction

The gases from the furnace are usually passed through a boiler in order to recover waste heat. During this phase some metals may condense and be recovered. The gases can then be cleaned from the dust by passing them through bag filters. The collected dust can be recycled. The sulphur which was contained in the sinter material fed to the blast furnace also goes into the gas stream as $SO_2$, but the $SO_2$ concentration is too low for removal. Consequently the gases are diluted with fresh air (also used as ventilation air) before de-dusting and then sent to the stack. Some 10 per cent of the total potential $SO_2$ emissions come from this source.

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56/ EPA Treatability Manual, Vol. II, Industrial Descriptions, United States Environmental Protection Agency, July 1980.

The waste slag produced during this operation and the sintering process is usually disposed of in a land disposal site.

5.1.4 Pollution control during lead bullion refining

The refining operations are usually carried out at relatively low temperatures. The only environmental hazard comes from the fumes which may originate. They contain lead and, in some cases, metals such as bismuth, cadmium, hallium, and arsenic as the main pollutants. Large volumes of ventilation air are usually used. This air is passed through bag filters before venting.

In electrolytic lead refining the main hazard is arsenic trioxide evolving from the bath into the off-gases. Therefore cooling must be provided to condense the arsenic trioxide before the gases are sent to the bag filters.

5.2 Retrofitting of existing plants to reduce pollution

The main environmental hazards posed by lead production facilities are $SO_2$ and dust emissions. Both can and have been successfully reduced in the past in existing plants. The first step in removing $SO_2$ from off-gases consists of changing the concentrated ore roasting technology by switching from down-draft to up-draft sintering machines. Then off-gases can be produced which are amenable to $SO_2$ removal. For those plants that are located in remote areas (sulphuric acid would be too costly to transport), it is possible to deliberately produce very diluted $SO_2$ gas streams which can then be dispersed by a tall stack. It is, however, well known that such lead smelters create pollution problems in the surrounding areas. For example, in one case air pollution extended for about five kilometers from the smelting site whereas soil pollution was detected for more than ten kilometers.[57/58/] Similarly, air and soil pollution around the Mezica mine and smelter (Yugoslavia) extended as far as ten kilometers and seven kilometers respectively.[59/60/]

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57/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

58/ Landrigan, P.J., S.H. Gelbach, B.F. Rosenblum, J.M. Shoults, R.M. Candelaria, W.F. Barthel, J.A. Liddle, A.L. Smrek, N.W. Staehling, and J.F. Sanders, (1975b) "Epidemic Lead Adsorption Near an Ore Smelter; The Role of Particulate Lead", New Engl. J. Med., 292:123-129.

59/ Djuric, D., Z. Kerin, L. Graovac-Leposavic, L. Novak, and M. Kop, Environmental Contamination by Lead from a Mine and Smelter; A Preliminary Report, Arch. Environ. Health, 23:275-279, 1971.

60/ Kerin, Z., Lead in New-Fallen Snow Near a Lead Smelter, Arch. Environ. Health, 26:256-260, 1973.

In 1974 the United States Environmental Protection Agency examined the six major lead production plants in the USA. They estimated that the economic impact of bringing them within federal control standards was expected to be 51 million dollars (although three of the plants were already equipped with acid plants).[61] This shows that also in this case pollution control is possible if sufficient resources are devoted to this purpose.

As for particulate emissions, existing plants can be relatively easily equipped with bag filters and other dust collecting equipment which can remove nearly 100 per cent of dust and fumes from off-gases.

5.3 Pollution control costs

An estimation of the economic impact on primary lead smelters caused by the compliance with strict environmental standards was made by the United States Environmental Protection Agency in 1974.[62] Both dust and $SO_2$ emission were considered and acid plant costs were included in the estimates. The results for model size plants are given in table 5.1.[63]

Table 5.2. Costs of control for selected model plants in the United States primary lead industry

| Model size (tons) | Investment ($US m) | | | Annualized cost ($US m) | | | Cost per ton of annual capacity | | |
|---|---|---|---|---|---|---|---|---|---|
| | expected | min | max | expected | min | max | expected | min | max |
| 107,000 | 8.9 | 4.3 | 12.5 | 2.1 | 1.0 | 3.0 | 17.8 | 8.8 | 26.3 |
| 131,000 | 9.9 | 5.1 | 13.8 | 2.5 | 1.2 | 3.4 | 17.4 | 8.3 | 23.6 |

Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

The costs are estimated for secondary smelters to be much lower since those plants were in a much more favorable situation from an environmental standpoint. The corresponding figures are given in table 5.3.

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61/ The Cost of Clean Air, United States Environmental Protection Agency, 1974.

62/ The Cost of Clean Air, Environmental Protection Agency, 1974.

63/ Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

Table 5.3. Costs of control for selected secondary lead plants

| Model tons/day | Investment ($US 000) expected | min | max | Annualized cost ($US 000) expected | min | max | Unit cost $US 1000/ton/day expected | min | max |
|---|---|---|---|---|---|---|---|---|---|
| 109 | 305 | 171 | 434 | 68.9 | 26.3 | 108.1 | 0.63 | 0.24 | 0.99 |
| 54 | 148 | 79 | 218 | 34.3 | 11.3 | 54.4 | 0.64 | 0.21 | 0.99 |
| 15.8 | 59 | 37 | 82 | 15.3 | 9.3 | 21.7 | 0.97 | 0.59 | 1.31 |

Source: Atkins, M.H. and J.F. Lowe, The Economics of Pollution Control in the Non-Ferrous Metals Industry, Pergamon Press, 1979.

A study carried out by Charles River Associates and the Research Corporation of New England for the Lead Industry Association estimated the impact of new air quality standards promulgated by the EPA in 1978 on the lead industry.[64/] Proposed compliance with the EPA 1.5 microg/$m^3$ (90 day average) standard for lead concentration in air was considered economically devastating.

Table 5.4. Impact of attempting to meet EPA ambient air lead standard

| Industry sector | Costs ($US) | | Plant closings |
|---|---|---|---|
| | Capital | Annual | |
| Primary smelting | 190 million | 35 million | All seven |
| Secondary smelting | 285 million | 60 million | 40 of 50 (90 per cent loss of capacity) |

Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, J. Cole: United States Environmental Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

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64/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, J. Cole: United States Environmental Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

5.4 Emission standards

The World Bank guidelines on pollutant concentrations in the gaseous effluents produced by lead smelters are as follows:[65]

Table 5.5. Presumptive limits for lead works

| | | |
|---|---|---|
| **Sulfur dioxide** | | |
| Inside plant fence | Annual arithmetic mean | 100 micro/$m^3$ |
| | Maximum 24-hour peak | 1,000 micro/$m^3$ |
| Outside plant fence | Annual arithmetic mean | 100 micro/$m^3$ |
| | Maximum 24-hour peak | 500 micro/$m^3$ |
| **Particulates** | | |
| | Annual geometric mean | 75 micro/$m^3$ |
| | Maximum 24-hour peak | 260 micro/$m^3$ |
| **Arsenic (as As)** | | |
| Inside plant fence | 24-hour average | 0.006 mg/$m^3$ |
| Outside plant fence | 24-hour average | 0.003 mg/$m^3$ |
| **Cadmium (as Cd)** | | |
| Inside plant fence | 24-hour average | 0.006 mg/$m^3$ |
| Outside plant fence | 24-hour average | 0.003 mg/$m^3$ |
| **Lead (as Pb)** | | |
| Inside plant fence | 24-hour average | 0.008 mg/$m^3$ |
| Outside plant fence | 24-hour average | 0.004 mg/$m^3$ |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

The limits imposed in the UK depend on the size of the plant, and consequently the amounts of gases emitted. Three classes are considered. The corresponding limits are reported in table 5.6.[66]

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65/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

66/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, A. Barbour: European Economic Community Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

Table 5.6. Air pollution limits for lead works, UK

| Works category | Gas volume | | Individual stack concentration* | | Total mass emission* | |
|---|---|---|---|---|---|---|
| | cu.ft./min. | $m^3$/min. | grains/ cu.ft. | $g/m^3$ | lbs/hour | kg/hour |
| Class I | >7,000 | 200 | 0.05 | 0.115 | 0.6 | 0.27 |
| Class II | 7,000-140,000 | 200-4,000 | 0.01 | 0.023 | 6.0 | 2.7 |
| Class III | >140,000 | >4,000 | 0.005 | 0.0115 | 12.0 | 5.4 |

* Measured as elemental lead

Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy and Environmental Control, A. Barbour: European Economic Community Laws and Regulations as Applied to the Lead and Zinc Industries, AIME, New York, 1979.

World Bank guidelines on pollutant concentrations in liquid effluents for primary lead smelters are as follows:[67/]

Table 5.7. Guidelines for permissible water pollutants from a primary lead smelter (kg/ton product)

| | Maximum 24-hour | Consecutive 30-day average |
|---|---|---|
| TSS | $4.2 \times 10^{-2}$ | $2.1 \times 10^{-2}$ |
| Cd | $8.0 \times 10^{-4}$ | $4.0 \times 10^{-4}$ |
| Pb | $8.0 \times 10^{-4}$ | $4.0 \times 10^{-4}$ |
| Zn | $8.0 \times 10^{-3}$ | $4.0 \times 10^{-3}$ |
| pH | 6-9 units | 6-9 units |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

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67/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

For secondary lead smelters the corresponding figures are:

Table 5.8. Guidelines for permissible water pollutants from a secondary lead smelter (kg/ton product)

| | Maximum 24-hour | Consecutive 30-day average |
|---|---|---|
| TSS | $5 \times 10^{-2}$ | $2.5 \times 10^{-2}$ |
| Cd | $4 \times 10^{-5}$ | $2.0 \times 10^{-5}$ |
| Pb | $1 \times 10^{-3}$ | $0.5 \times 10^{-3}$ |
| As | $1 \times 10^{-4}$ | $0.5 \times 10^{-4}$ |
| pH | 6-9 units | 6-9 units |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

## 5.5 Health protection for workers

Lead is well known to produce acute and long-term poisoning, especially in workers in the lead industry. Smelting and refining operations have the greatest potential for hazardous exposure. In recent years lead poisoning has decreased noticeably among those workers due to safer handling procedures, better worker protection at the workplace, and automation which has reduced the need for the worker's presence during some production phases.

Lead poisoning occurs by inhalation, ingestion, or absorption through the skin. On the average, 30 $\pm$ 10 per cent of inhaled lead is absorbed by the organism. About 5-10 per cent of the ingested lead is also absorbed.[68/] The lead so metabolized can cause long term effects since the biological half-time of lead is generally accepted to be longer than ten years.[69/] The nervous system is especially affected by lead. Health effects can be correlated to lead concentration in the blood. The present no-detect-effect level for subclinical neuropathy is 40-50 microg/100 ml. Noticeable brain

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68/ "Environmental Health Aspects of Non-Ferrous Metals: Cadmium, Copper, Lead, Nickel and Zinc", UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO, United Nations Environment Programme.

69/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

dysfunctions start at a concentration of 60-70 microg/100 ml. In evaluating health effects the following guideline may be useful: if the blood lead level is used as a measure of lead absorption then continuous exposure to 1 microg/$m^3$ of lead in air would contribute to lead levels of about 1-2 microg/100 ml of blood.[70] For this reason the occupational exposure limit for airborne lead is rather low in most countries. Table 5.8 presents some of these values.[71]

Table 5.9. Occupational exposure limits for airborne toxic substances

| | | | | | USA | | |
|---|---|---|---|---|---|---|---|
| | Fed. Rep. Germany | Japan | Sweden | USSR | Occupational standard | ACGIH TWA | ACGIH Short term |
| Lead and inorganic compounds, mg/$m^3$ | 0.2 | 0.15 | 0.1 | 0.01 | 0.2 | 0.15 | 0.45 |

Source: ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

Hazards to workers can nevertheless be very serious. For example, the lead concentration in the air was measured for different operations in a typical lead ore smelter in Salt Lake City, Utah, (USA). These data are reported in table 5.10[72] They clearly indicate that lead concentrations were extremely high with potential health hazards to the workers who were, in fact, required to use respirators.

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70/ "Lead, Executive Summary", Environmental Health Criteria 3, WHO, Geneva, 1983.

71/ "Environmental Health Aspects of Non-Ferrous Metals: Cadmium, Copper, Lead, Nickel and Zinc", UNEP Workshop on the Environmental Aspects of Non-Ferrous Metals Industries, WHO, United Nations Environment Programme.

72/ "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

Table 5.10. Air lead concentrations in three primary lead smelters (microg/m$^3$)[a]

| Smelter | Year | Location[b] | Means[c] | Mean of means | Range (all values) |
|---|---|---|---|---|---|
| A | 1972-75 | (1) | 610, 1930, 2860 | 1800 | 250-3670 |
| | | (2) | 970, 470, 450 | 630 | 250-1380 |
| | | (3) | 860, 950, 320 | 710 | 200-1700 |
| | | (4) | 1220, 350, 950 | 840 | 260-1640 |
| B | 1973-74 | (1) | 1310, 2330, 4720 | 2790 | 370-5160 |
| | | (2) | 2740, 3460, 770 | 2320 | 310-7570 |
| | | (3) | 860, 140, 530 | 510 | 120-1560 |
| | | (4) | 1270, 540, 5730, 4050 | 2900 | 60-7220 |
| C | 1973-74 | (1) | -- | -- | -- |
| | | (2) | 3850, 8740, 830 | 4470 | 10-31 200 |
| | | (3) | 1320, 230 | 780 | 90-1340 |
| | | (4) | 80 | 80 | |

[a] Data provided by M. Varner, American Smelting and Refining Co., Salt Lake City, Utah, USA.

[b] Locations: (1) Ore proportioning; (2) nodulizing and sintering; (3) blast furnace; (4) drossing and reverberation.

[c] Determined with personal monitors on separate occasions. Each sampling period was 5-7 hours.

Source: "Lead", Environmental Health Criteria 3, WHO, Geneva, 1977.

Similar data are not available for secondary smelters, but some studies seem to indicate that workers are indeed exposed to high lead levels in air which then results in increased blood lead levels.

# 6. ZINC

## 6.1 Pollution control technologies for zinc production plants

### 6.1.1 Pollution control during mining

Treatment and disposal of mine water is the main problem at this stage. This water is muddy and contaminated with particulate matter with potentially large fluctuations in its density and quality. Since mine water is usually acidic, its pH can be raised by adding limestone. This is especially beneficial if the water is going to be recycled to the ore processing plant, since the flotation operation for zinc and lead-zinc ores is typically run at elevated pH values (between 8.5 and 11). In this case, though, the suspended solids must first be removed. The water which cannot be recycled can be disposed of after treatment.

A good example of such a technology is given by the Tochibora Mine. Since the original lead/zinc-containing rock is rich in limestone, the pH value of the groundwater is already somewhat in the alkaline range (7-8). Moreover, it contains few dissolved ions. By removing the suspended solids the mine wastewater can be used as industrial water at the nearby Shikama lead-zinc plant. Some 60 per cent of the Shikama plant is supplied by the Tochibora mine.[73/]

### 6.1.2 Pollution control during ore processing

Dust emissions during grinding operations can be reduced by wetting the ore and encasing the grinding equipment. A much more serious problem during ore processing is caused by tailings and water disposal from the flotation operations. The tailing slurry is first sent to thickeners where the solids settle. These solids are then sent as a thick slurry to lagoons or impoundment areas. The thickener overflow can be recycled and used again for bulk flotation. The overflows from other flotation/thickening steps can also be recycled. However, some amounts of harmful impurities, consisting mainly of flotation agents, are contained in these streams and must be removed. Methods to remove these contaminants have been devised. For example, the Ion, Precipitation, and Ultra Fine (IPU) flotation process utilizes sulphuric acid, sodium sulphide, acofloc (a flocculant) and methyl-isobutyl-ketone additions to precipitate the impurities, which are then separated by filtration. The water can be recycled. This system has been used at the Shikama plant, resulting in a remarkable improvement of the total effluent quality, substantial savings of floatation reagents, and additional recovery of zinc and even copper (as by-product) from the wastewater.[74/]

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73/ Matsui, N., "Pollution Preventive Measures in a Lead-Zinc Mine in Japan", UNEP Industry and Environment, Vol. 8, No. 1, January, February, March 1985.

74/ Ibid.

### 6.1.3 Pollution control during smelting

Pollution control during the roasting-electrolytic process

During the roasting step the main environmental hazard comes from the roaster off-gases, which contain $SO_2$, dust and fumes, and also vapors from heavy metals such as mercury, cadmium, and arsenic (originally present in the bore concentrate). In relatively modern plants a waste heat boiler is used to recover energy and cool down the roaster off-gases. Dust and fumes are then removed by passing them through cyclones and then, for a more complete removal, also through an electrostatic precipitator. In older plants utilizing low-efficiency roasters (such as the multi-hearth roasters) the $SO_2$ concentration in the gases is too low for removal and the gases are sent directly to a stack. In modern plants using fluidized bed roasters the $SO_2$ can be as high as 9.5 per cent, as in the new (1979) Jersey Miniere Zinc Company plant at Clarksville, Tennessee (USA).[75] Then the $SO_2$ can be converted efficiently to sulfuric acid.

Before $SO_2$ removal, the off-gases from the electrostatic precipitator must be cleaned from their heavy metal content. The gases are first scrubbed in Venturi scrubbers and then passed in a mercury-removal Boliden-Norzink tower where a mercuric chloride solution flows counter current. Mercury in the gas reacts with the solution forming mercurous chloride, which precipitates and is later removed by flotation. The heavy-metal free gas stream can then be treated in a sulphuric acid plant where conversion to $H_2SO_4$ takes place. The clean gases are usually vented through a stack.

In the second part of the process the potential environmental hazards come mainly from the zinc leaching operation. The leach residue produced during this operation contains all the insoluble solid materials present in the calcine plus some electrolyte solution. The residue is collected at the bottom of the thickeners as a slurry, after flocculation. It is then treated with lime to remove the excess acidity, washed and filtered. The final washed acid leach residue cake is then sent to an impoundment area or a lagoon. The environmental problems are complicated by the presence of heavy metal residues.

Pollution control during the pyrometallurgical process

The roasting operation is, in principle, similar to that used in the electrolytic process. Consequently it poses the same type of environmental problems. However, in the pyrometallurgical process the roasting phase is also a sintering phase, i.e. the end product must not only be fully calcined, but also have a minimum lump size in order to meet the requirements for the subsequent reduction step. This implies that about 80 per cent of the product from the sintering machine must be recycled as dust.[76] Therefore, in

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75/ "Lead-Zinc-Tin 80", TMS-AIME World Symposium on Metallurgy & Environmental Control, L. Painter: The Electrolytic Zinc Plant of Jersey Miniere Zinc Company at Clarksville, Tennessee, AIME, New York, 1979.

76/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

addition to standard off-gas cleaning, a very large volume of ventilation air must also be extracted and cleaned from dust. Bag filters, cyclones or Venturi scrubbers can be used for this purpose.[77] The off-gases should then undergo heavy metal removal before being sent to the sulphuric acid plant for $SO_2$ removal.

The environmental problems associated with the next phase, i.e. sinter reduction, depend strongly on the type of equipment used. The Imperial Smelting Process is much more environmentally sound than horizontal retorts. The zinc contained gases produced during the reduction phase are almost completely recovered by the lead splash rotor. The escaping zinc vapors are condensed by passing the gases through wet scrubbers. During this operation the other heavy metals are also removed. The gases can then be vented.

The liquor obtained from the scrubber contains the heavy metals from the gases. Upon addition of lime to the liquor these metals are precipitated, settled in thickeners, dewatered and then reprocessed for recovery. The liquor is mostly recycled to the scrubber. Only a part is discharged after treatment. The slag produced from the ISP is granulated and dumped or used as an aggregate in concrete.

### 6.1.4 Pollution control during zinc refining

At this stage the main environmental hazard consists of potential fume emissions containing heavy metals, especially cadmium. Provided that a good fume collection system exists, removal of heavy metals is carried out using scrubbers as described in the previous section.

### 6.1.5 Pollution control during the hydrometallurgical process

As in the electrolytic process, sludge disposal after leaching constitutes a potential environmental problem. Effluent production is minimized by recycling. The excess is treated to remove heavy metals prior to discharge. The sludge can be impounded in leak-proof areas.

## 6.2 Retrofitting of existing plants to reduce pollution

For those plants which utilize obsolete or older production technologies, remedial actions are difficult. These plants may also suffer from low efficiency and high production costs and are destined to be phased out with time. As an example, in the USA between 1969 and 1978, six out of eight primary zinc smelters utilizing the horizontal or vertical retort smelting process closed down. One was converted to the electrolytic process and the other one was still in operation in 1979.

Replacing technologies, at least in some parts of the plant, may be beneficial from both an economic and environmental standpoint. For example, modern roasters not only do not require any supplementary fuel for their operation, but also produce rich $SO_2$ streams which can be much more

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77/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

effectively converted to sulfuric acid. Technologies now exist to control heavy metal emissions, especially mercury. Boliden-Norzink columns have been proved to perform very satisfactorily. In pyrometallurgic smelting the ISP is already environmentally sound provided that pollution control devices are utilized to control final gaseous emissions. Additional pollution control equipment can be considered to be independent from the furnace and can be retrofitted to existing plants.

## 6.3 Pollution control costs

One important source of information on pollution control costs in the zinc industry is a publication of the United States Environmental Protection Agency concerning the situation in the USA.[78] In 1971 the EPA estimated that all the United States primary zinc smelters (producing over one million tons/year) emitted 263,000 tons of $SO_2$ and 18,600 tons of particulate. At that time no emission control existed for $SO_2$ and only 90 per cent of the total particulates produced in the smelting operation were collected prior to off-gas discharge into the atmosphere. By 1979 the EPA forecast that the corresponding figures would be 1,900 tons for $SO_2$ and 31,000 tons for particulate emissions, thanks to the adoption of control technologies. The associated investment costs were estimated to be $US 32.4 million with total annual operating costs of $US 8.15 million (1974 prices). More detailed information is reported in table 6.1 for different plant sizes.[79]

Table 6.1. Costs of pollution control for United States primary zinc producers

| Model size (tons) | Investment ($US million) | | | Annual operating cost ($US million) | | | $US/t/year | Unit cost | |
|---|---|---|---|---|---|---|---|---|---|
| | expected | min | max | expected | min | max | expected | min | max |
| 91,000 | 8.67 | 6.66 | 11.1 | 2.17 | 1.65 | 2.77 | 23.8 | 18.1 | 30.4 |
| 139,000 | 11.6 | 8.82 | 15.0 | 2.91 | 2.23 | 3.76 | 20.9 | 16.0 | 27.1 |
| 149,000 | 12.2 | 9.42 | 15.6 | 3.09 | 2.37 | 3.97 | 22.2 | 17.1 | 28.6 |

Source: The Cost of Clean Air, Environmental Protection Agency, Senate Document No. 93-122, 1974.

78/ Atkins, M.H. and J.F. Lowe, "The Economics of Pollution Control in the Non-Ferrous Metals Industry", Pergamon Press, 1979.

79/ Ibid.

For the secondary zinc industry, the estimated investment costs for various model plant sizes are given in table 6.2.

Table 6.2. Costs of pollution control for United States secondary zinc producers

| Model size capacity (tons) | Investment ($US 000) | | | Annualized cost ($US 000) | | | Unit cost $US/t/year | | |
|---|---|---|---|---|---|---|---|---|---|
| | expected | min | max | expected | min | max | expected | min | max |
| 4,990 | 138 | 80.4 | 195 | 43.2 | 22.5 | 64.4 | 7.85 | 4.09 | 11.7 |
| 10,990 | 225 | 131 | 345 | 12.3 | 386 | 113 | 6.03 | 3.22 | 9.42 |

Source: The Cost of Clean Air, Environmental Protection Agency, Senate Document No. 93-122, 1974.

6.4 Emission standards

According to reference[80] the maximum acceptable emissions into the air for zinc plants are the same as for lead plants. These standards have already been given in the lead chapter section 5.10. For liquid effluent standards, the limits set by the United States Environmental Protection Agency are reported in table 6.3.[81] The standards for primary zinc production plants are reported in table 6.4 in terms of kg of pollutant per ton of metal produced.

80/ "Development Document for Interim, Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061 Vol. I & II, Washington, D.C., October 1975.

81/ "Processes, Procedures, and Methods to Control Pollution from Mining Activities", United States Environmental Protection Agency, EPA-430/9-73-011, Washington, D.C., October 1973.

Table 6.3. Guidelines for permissible water pollutants from a primary zinc smelter (mg/l)

| | Concentration (mg/l) in effluent | |
|---|---|---|
| | 30-day average | 24-hour maximum |
| pH | 6-9 units | 6-9 units |
| TSS | 20 | 30 |
| Cyanide | 0.01 | 0.02 |
| Cd | 0.05 | 0.1 |
| Cu | 0.05 | 0.1 |
| Hg | 0.001 | 0.002 |
| Pb | 0.2 | 0.4 |
| Zn | 0.2 | 0.4 |

Source: "Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", United States Environmental Protection Agency, EPA 440/1-75/061 Vol. I and II, Washington, D.C., October 1975.

Table 6.4. Guidelines for permissible water pollutants from a primary zinc smelter (kg/ton zinc)

| | Maximum 24-hour | Consecutive 30 day average |
|---|---|---|
| TSS | 0.42 | 0.21 |
| As | $1.6 \times 10^{-3}$ | $8 \times 10^{-4}$ |
| Cd | $8.0 \times 10^{-3}$ | $4 \times 10^{-4}$ |
| Se | 0.08 | 0.04 |
| Zn | 0.08 | 0.04 |
| pH | 6-9 units | 6-9 units |

Source: "Environmental Guidelines", Office of Environmental Affairs, The World Bank, July 1984.

## 6.5 Health protection for workers

Zinc is relatively non-toxic. The most common worker intoxication from zinc is by fume inhalation during operations such as smelting or galvanizing or in any other where zinc is heated at high temperature. The result is metal fume fever, a disorder from which the worker usually recovers within 24 to 36 hours. It has been shown that occupational exposures to zinc oxide fumes in the range of 3-15 $mg/m^3$ for 2 to 35 years did not produce detrimental effects.[82] In some workplaces concentrations up to 100 $mg/m^3$ and even higher have been found.[83] Adequate ventilation should be provided to reduce these values below the occupational exposure limit adopted in each country. Some selected values are reported in table 6.5.

Table 6.5. Occupational exposure limits for airborne zinc, $mg/m^3$

| | | | | | USA | | |
|---|---|---|---|---|---|---|---|
| | Fed. Rep. Germany | Japan | Sweden | USSR | Occupational standard | TWA | ACGIH Short term |
| Zinc chloride (fumes) | | | 1 | | 1 | 1 | 2 |
| Zinc oxide (fumes) | 5 | 5 | 1 | 6 | 5 | 5 | 10 |

Source: Occupational exposure limits for airborne toxic substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

More serious toxic effects can be produced on the workers by exposure to cadmium, a by-product of zinc manufacturing. Cadmium can produce acute and long-term effects, especially on the lungs and kidneys. Exposure for eight hours to air containing 5 $mg/m^3$ may be lethal.[84] Toxic effects may result from exposure to cadmium levels in air of 1 $mg/m^3$. For this reason the occupational exposure limits adopted in many countries are rather low. These limits are reported in table 6.6.

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82/ Occupational Exposure Limits for Airborne Toxic Substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

83/ Ibid.

84/ Ibid.

Table 6.6. Occupational exposure limits for airborne cadmium, $mg/m^3$

| | Fed. Rep. Germany | Japan | Sweden | USSR | USA Occupational standard | USA TWA | USA ACGIH Short term |
|---|---|---|---|---|---|---|---|
| Cadmium dust and soluble salts (as cadmium) | | | 0.5 | | | 0.5 | 0.15 |
| Cadmium oxide (fumes as cadmium) | 0.1 | 0.1 | 0.02 | 0.1 | TWA/M[a] 0.1/3 | M[a] 0.05 | 0.05 |

[a] M = ceiling value

Source: Occupational exposure limits for airborne toxic substances, ILO, Occupational Safety and Health Series No. 37, Geneva, 1977.

# 7. TIN

## 7.1 Pollution control technologies for tin production plants

### 7.1.1 Pollution control during mining

Because of the different types and locations of tin mines the environmental implications of the mining operations can be rather various. Underground mining of hard rock has a limited impact in comparison to open-pit mining. The problems associated with open-pit mines are mainly dust generation from blasting and earth moving operations, and deforestation. They can be partially circumvented by water spraying the dust generating areas, and by implementing an appropriate program of land reclamation and revegetation.

More serious problems are encountered in alluvial tin placers especially in southeast Asia where mine areas compete for land with other activities such as agriculture, forestry, and husbandry. So far the mined areas have not been extensively reclaimed. In principle it is feasible to put the tailings back into the mine and start immediate fertilization and revegetation (legumes are an optimal choice) with consequent full reclamation of the mined areas. A major obstacle in this direction is the fact that the alluvional placers are never completely worked out and further expolitation may continue in different periods, according to the fluctuation of the tin prize and the overall world tin supply.[85/]

### 7.1.2 Pollution control during ore processing

For the case of alluvial tin deposits the separation of cassiterite ore from gangue is just a physical operation. Consequently no major chemical pollution problems arise, but a large amount of tailings must be disposed of. This creates unsightly waste piles, tailings areas, and muddy rivers. This problem cannot be fully overcome, but can be partially circumvented by an appropriate land use and management plan coupled with reclamation programs.

The disposal of tailings is also the major problem encountered during hard rock ore processing. In addition to simple gravity separation the ore may sometimes be processed by flotation of the gangue. In such a case the process water has not only a high content of suspended solids, but may become contaminated by chemical agents. Water should then be recycled and the excess water should be treated with lime in order to neutralize the potentially hazardous dissolved chemicals, before discharge into the environment.

### 7.1.3 Pollution control during smelting of higher-grade tin concentrates

The gases evolving from the concentrate smelting furnace and from the slag smelting furnace contain large amounts of dust (e.g. 50-150 g/Nm$^3$ of gas in electric smelting).[86/] These gases are either cooled with cooling

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85/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, J. Harris: The Problems of Tin, AIME, New York, 1979.

86/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

water or by passing them through waste heat boilers. They are then sent to dust collecting equipment usually consisting of Venturi wet scrubbers or multi-compartment baghouses where most of the dust is removed. Final dust removal may be accomplished with electrostatic precipitators. Traditionally, tin smelters have always made sure that the off-gas particulate emission is very low. In fact the dust contains a large fraction of the total tin processed (as high as 10 per cent of the charge for both furnaces) which can be conveniently recovered and recycled.

Smelter off-gases are also rich in CO and $H_2$ since a reducing atmosphere must be maintained in the furnace at all times. Therefore, the gases are flared off rather than simply being released through a stack. Depending on the charge composition the gases may also contain variable amounts of $SO_2$. In most circumstances this concentration is too low to permit conversion to sulphuric acid and the $SO_2$ is released into the environment.

### 7.1.4 Pollution control during smelting of lower-grade tin concentrates

Processing lower-grade ore often means processing hard rock ore containing large amounts of pyrites. Most of their sulphur content is then released during the preliminary roasting operation. If multiple-hearth roasters are used the $SO_2$ generated is not amenable to sulphuric acid conversion. This may create the typical environmental problems associated with $SO_2$ emissions. Higher $SO_2$ concentrations can be obtained only using modern roaster design or using ore fuming processes. In this case $H_2SO_4$ conversion plants can be successfully operated.

The leaching operation, often associated with roasting, may result in the contamination of the leaching liquor with elements such as arsenic, lead, and bismuth. These elements are recovered from the liquor by precipitation with lime and then reprocessed. The environmental problems and control technologies associated with the actual smelting operaton are similar to those described in the previous section. The slag fuming operation is also a potential source of emissions. The fumes and dusts evolved have a high economic value because of their metal content (about 50 per cent tin). The exhaust gas may also contain recoverable amounts of $SO_2$ (e.g. 8 per cent in the modern SIROSMELT type of furnace)[87] which can be treated in sulphuric acid conversion plants.

### 7.1.5 Pollution control during crude tin refining

Most tin refining operations present minimal environmental hazards. A noticeable exception is the removal of arsenic using aluminium. Although arsine is formed only if the resulting AlAs is contacted with water, many smelters now prefer to use sodium instead of aluminium during this operation, in order to rule out any possibility of incidents. In acid electrolysis the

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87/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium on Metallurgy & Environmental Control, K. Foo and J. Floyd: Development of the Matte Fuming Process for Tin Recovery from Sulphide Materials, AIME, New York, 1979.

electrolytic bath contains phenol or cresol-sulphonic acids which may give rise, in principle, to hazardous emissions and fumes. This problem is usually minimized by the use of low temperatures and good ventilation. If alkaline baths are used the process is more efficient, since a higher impurity content in the crude tin is accepted. On the other hand, the electrolysis must be carried out at a temperature of 80°C and the emission problems may become more important. Good ventilation and hooding is then required.

7.2 Retrofitting of existing plants to reduce pollution

Plants processing higher-grade concentrates have limited emission problems since nearly 100 per cent of the dust and fumes is already recovered in order to recycle their tin content. Moreover, $SO_2$ emissions are usually very low. Plants processing lower-grade tin concentrate (from ore processing to final metal) have been faced with the need to boost their productivity and decrease the amount of discarded waste material. Because of the inefficiency associated with the traditional cassiterite ore concentration process the general trend has been to retrofit existing plants with tin concentrate fuming furnaces which can produce a medium-grade concentrate (40-50 per cent tin) at high recovery rates (over 90 per cent). By comparison, mineral processing can give slightly better concentrates (about 60 per cent tin), but much lower recovery rates (about 50 per cent).[88/] This has not only economic implications, but also environmental consequences, since the amount of tailings to be disposed of is much lower. In some cases, fuming may even replace ore processing altogether.[89/] A disadvantage of the concentrate fuming process is that $SO_2$ is generated. On the other hand, if the proper technologies are employed the $SO_2$ generated will have a concentration in the off-gases which is high enough for sulphuric acid conversion.

7.3 Pollution control costs

For the case of tin smelters, the equipment used for dust removal from off-gases can be considered as either pollution control equipment or process equipment, because of the valuable tin content of the dust. Data concerning the cost of dust collecting units have already been presented in the copper chapter. Data concerning the cost of $SO_2$ removal were also given there.

A comparison of the main characteristics of the different tin smelting furnaces is given in table 7.1. The information contained in this table can be used to evaluate the performance of each type of furnace and hence the associated environmental costs (based on a first estimation of the size of the gas cleaning devices and their operating costs).

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88/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, T.R.A. Davey: Advances in Lead, Zinc and Tin Technology-Projections for the 1980's, AIME, New York, 1979.

89/ "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, S. Pearce: Development in the Smelting and Refining of Tin, AIME, New York, 1979.

7.4 Emission standards

The types of pollutants released by tin smelters vary depending on the technology used and the pollutant concetration in the tin concentrate processed. The gaseous emission limitations for some of the potentially relevant pollutants for this case (such as $SO_2$, CO, As, Pb and particulates) are given in table 7.2.[90/]

7.5 Health protection for workers

Inhalation of elemental tin does not produce any effect in man.[91/] Prolonged exposure to tin oxide dust and fumes can result in stannosis, a benign pneumoconiosis which is characterized by small shadows in the pulmonary x-ray picture. This disorder may develop after extensive exposure (at least 3-5 years), but does not produce any impairment of the pulmonary function, provided that other agents, such as silica, are not present in the inhaled dust. More than 200 cases of stannosis have been described in the literature.[92/93/94/] Worker exposure to tin or tin oxide fumes is mainly associated with operations such as bagging of concentrate, mixing of furnace charge components, furnace tapping, and periodic cleaning of bag filters. Some refining operations may also result in exposure to tin fumes. It has been reported that no cases of stannosis were observed in workers exposed to tin oxide dust concentrations of 10 $mg/m^3$ for ten years. Nevertheless, the generally accepted maximum allowable concentration of $SnO_2$ in the working environment is considered to be 2 $mg/m^3$ of air.[95/]

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90/ Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

91/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

92/ Schuler, P., E. Cruz, C. Guijon, V. Maturana, and A. Valenzuela, Stannosis, Benign Pneumoconiosis Owing to Inhalation of Tin Dust and Fume, II, Clinical Study, Ind. Med. Surg., 27:432-435, 1958.

93/ Robertson, A.J. and P.H. Whitaker, Radiological Changes in Pneumonconiosis due to Tin Oxide, J. Fac. Radiol., 6:224-233, 1957.

94/ Pendergrass, E.P. and A.W. Pryde, Benign Pneumoconiosis due to Tin Oxide, J. Ind. Hyg., 30:119-123.

95/ "Tin and Organotin Compounds", Environmental Health Criteria 15, WHO, Geneva, 1980.

Table 7.1. Comparison of tin reduction furnaces

| | Rotary furnace | Reverbatory furnace | Electric furnace |
|---|---|---|---|
| Smelting time (h/t charge) | 0.7 | 0.48 | 0.48 |
| Temperatures (°C) | 1100 | 1350 | 1580 |
| Throughput ($t/m^2d$) | 1.36 | 1.0 | 6.6 |
| Furnace operation (days/year) | 300 | 300 | 330 |
| Refractory life (months) | 8 | 8<br>2 years: walls and roof | >36 |
| Fuel oil (l/h) | 200 | 200 | --- |
| Reductants (kg/t metal) | 330 | 370 | 220 |
| Power consumption (kWh/t metal) | 208 | 126.9 | 1580 |
| Cooling water ($m^3$/t metal) | 5.88 | 0.2 | 18 |
| Tin recovery (percentage) | 98.5-99.0 | 99.0 | 99.5 |
| Waste gas ($m^3$/t charge) | 6500 | 16,000 | 250 |
| Dust, max. (percentage) | 10 | 10 | 5 |

Source: "Lead-Zinc-Tin '80", TMS-AIME World Symposium of Metallurgy & Environmental Control, F. Oberbeckmann and M. Porten: Tin Smelting at Berzelius, Duisburg, AIME, New York, 1979.

Table 7.2 Guidelines for emission levels in tin smelter off-gases

| | | |
|---|---|---|
| Sulfur dioxide ($SO_2$) | | |
| Inside plant fence | Annual arithmetic mean | 100 microg/$m^3$ |
| | Maximum 24-hour peak | 1000 microg/$m^3$ |
| Outside plant fence | Annual arithmetic mean | 100 microg/$m^3$ |
| | Maximum 24-hour peak | 500 microg/$m^3$ |
| Particulates | Annual geometric mean | 75 microg/$m^3$ |
| | Maximum 24-hour peak | 260 microg/$m^3$ |
| Carbon monoxide (CO) | Maximum 8-hour average | 10 microg/$m^3$ |
| | Maximum 1-hour average | 40 microg/$m^3$ |
| Lead (as Pb) | | |
| Inside plant fence | 24-hour average | 0.008 mg/$m^3$ |
| Outside plant fence | 24-hour average | 0.004 mg/$m^3$ |
| Arsenic (as As) | | |
| Inside plant fence | 24-hour average | 0.006 mg/$m^3$ |
| Outside plant fence | 24-hour average | 0.003 mg/$m^3$ |

Source: Environmental Guidelines, Office of Environmental Affairs, The World Bank, July 1984.

## 8. CONCLUSIONS AND RECOMMENDATIONS

(a) The non-ferrous metal industries considered in this work are a major source of environmental pollution. The extent of the environmental impact produced by these industries depends largely on the type of metal processed, the location of the plant and/or mine, the process technology adopted, and the pollution control system used.

(b) Mining activities are likely to have a detrimental impact on the environment especially if they are located near populated areas. During open-cast mining the overburden material is often piled up in dumping areas near the mine. Whenever possible this material should be re-used as infill or stockpiled for later rehabilitation of the mined area followed by reforestation.

(c) Strip mining and exploitation of alluvial tin placers especially in Southeast Asia should be immediately followed by backfilling procedures aimed at reclaiming the strip-mined areas while the mining operation advances further. Revegetation eventually followed by agricultural and other husbandry activities can then begin within a few years.

(d) Underground mining is likely to have a more limited environmental impact than other types of mining operations. The problem associated with the disposal of gangue material still exists, but it can sometimes be solved by backfilling operations.

(e) Mining activities are also likely to produce dust, noise, and noxious emissions of blasting fume residues. Dust emissions should be controlled by water spraying the dust generating areas (such as broken ore at mining stopes, or blast holes), building paved haulage roads, and using appropriate methods to reduce the dust produced by blasting (such as using steam-air jets for mist generation). The noise and dust levels near the mine can be effectively reduced by tree belts or artificial screens built with waste rocks and material. When feasible, ventilation should be provided, or predominant winds should be taken into consideration when choosing the blast points, in order to promote the dispersion of the noxious fumes resulting from blasting operations.

(f) In non-arid regions contamination of mine water can be a serious environmental problem. The water used during mining operations (such as the water used in drilling in underground mines) or the mine run-off water (especially in open-pit mines) may become contaminated with chemical species originally present in the ground. This may result in highly acidic water in open-pit mines or alkaline water in underground mines. Dissolved metals may also be present. Provisions should be made to (a) estimate in advance the type and amount of pollutants contained in the mine water, (b) estimate the water flow produced, (c) collect the water before it escapes into the environment, and (d) build water treatment plants capable of removing suspended solids, neutralizing the excess acidity of alkalinity, and precipitating the dissolved metals prior to the discharge of the water into the environment.

(g) Dust is generated also during some ore processing operations such as loading, unloading, transporting, crushing and grinding the ore. Provision should be made to reduce the amount of dust produced, by water sprinkling. During transportation the humidity content of the ore should be kept at a

level which hinders dust formation. In order to decrease the dust concentration in the processing areas the dust generating operation should be identified and confined in appropriate rooms or spaces, the equipment should be sealed, and local ventilation should be provided. These recommendations should be even more strictly followed if the ore contains heavy metals such as lead or cadmium and antimony which constitute a health hazard by themselves.

(h) Concentrating metals in the sulphide ores (nickel, copper, lead, zinc, and tin) involves flotation. This practice requires very large amounts of water which becomes contaminated with variable amounts of flotation agents. These agents are often very toxic and contain cyanides. Consequently, the greatest efforts should be made in order to recycle the largest amount of flotation water (after tailings separation). Whenever possible less toxic flotation agents should be used, and research efforts should be directed toward their development.

(i) Tailings disposal after ore concentration can create a very negative environmental impact because of the amount of tailings produced by the industry, and because of their pollutant content resulting from previous operations (such as flotation). The safest way to dispose of these tailings consists of their impoundment in carefully selected areas, followed by revegetation. The impoundment areas should be located away from water sources, and should be impervious to seepage (i.e. the basin floor should be made of natural clay or artificial sealants).

(j) The concentration of most oxide ores and especially bauxite for alumina production requires a leaching operation. Both alkali (as in bauxite, and some nickel ore processing) and acids (as in some other nickel, copper and zinc ores) are used. The gangue material which is not solubilized during the process is removed and must be disposed of. This often creates an environmental impact, because of the residual alkali or acid content of the tailings. Impoundment in sealed basins is again the most acceptable disposal method which may or may not be followed by neutralization with lime, for the acid tailings case. Many alumina plants already utilize the method of total impoundment of the tailings, where the process and bauxite residues (red mud) lakes are integral parts of the process. Whenever possible this technology should be adopted. It has been proven that the practice of red mud disposal at sea is very detrimental to aquatic life. This practice should be replaced in the shortest time possible by more environmentally sound disposal methods.

(k) The pyrometallurgical smelting process used to produce the crude metal (such as nickel, copper, lead and zinc) from the sulphide ore concentrate involves the removal of the sulphur, originally contained in the concentrate, in the form of gaseous sulphur dioxide ($SO_2$). If released into the atmosphere $SO_2$ is eventually converted into sulphuric acid with the well known environmental consequences produced on human health, vegetation, and building by the phenomenon of the acid rain. The concentration of sulphur dioxide in the metal ore smelting furnace off-gas stream, and the amount of off-gases produced depends widely on the technology used. Older plants tend to produce more abundant gaseous emissions characterized by a low $SO_2$ concentration. Sulphur dioxide removal from such emissions is not economically viable. More modern plants produce $SO_2$-rich off-gases. In such a case it is possible to remove $SO_2$ from the off-gases and convert it into sulphuric acid, which is then sold. It is therefore recommended that smelters which produce off-gas streams with a high enough $SO_2$ concentration be retrofitted (if not already equipped) with an $SO_2$ conversion plant for

sulphuric acid production. Older plants should be eventually either phased out or revamped with more modern equipment capable of producing off-gas streams amenable to sulphuric acid conversion.

(l) Smelters also produce large amounts of dust and fumes which may escape with the off-gases. It is recommended that new plants be equipped with high efficiency dust collecting equipment and that older plants be retrofitted with similar equipment. This move may prove to be advantageous also from an economic point of view since the dust collected often contains metal oxides which can be recycled to the smelting furnace.

(m) Emissions from electrolytic aluminium smelters contain fluorides as pollutants. Similarly, plants for the electrolytic production of other metals (such as tin or copper) may also emit mists which contain pollutants. It is recommended that such plants be equipped with appropriate ventilation systems fitted with particulate collection equipment.

(n) In recent years several new processes have emerged for the pyrometallurgical smelting of nickel, copper, lead, zinc and tin. These processes offer several advantages such as higher metal recovery rates, higher concentration of sulphur dioxide in the off-gases (and consequent amenability to its conversion to sulphuric acid), reduced amounts of dust and fumes produced, higher energy efficiency, and the potential for smelting complex ores. The environmental aspects should play a decisive role in the choice of the smelting process for new plants. Countries are recommended to implement more stringent and better enforced environmental standards.

(o) Recycling and re-smelting of several metal scraps is already extensively practiced for lead, aluminium, copper, and to a lesser extent, tin, zinc and nickel. The percentage of metals produced by reprocessing scrap is expected to grow appreciably in the near future as a consequence of lhe cost increase of the primary metal production and the reduced energy cost associated with the secondary production.